Oxygen Transfer Phenomena in Activated Sludge

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Abstract

This dissertation investigates the impact of activated sludge on oxygen transfer in activated sludge plants. The effect of surfactants on oxygen transfer is also studied and a method to determine the floc volume of activated sludge is developed. The α-factor, i.e. the relationship of wastewater to clean water oxygen transfer coefficient, is chosen to enable comparison of oxygen transfer coefficients. The main results are summarized as follows:

- The floc volume significantly influences oxygen transfer and sedimentation of activated sludge. Oxygen transfer is reduced and sedimentation hindered with increasing floc volume. Floc volume influences oxygen transfer in coarse and fine bubble aeration systems in a similar fashion. This is in marked contrast to the effects of surfactants on oxygen transfer.
- The mixed liquid suspended solids concentration is an incorrect parameter for comparing phenomena related to the floc volume. Better correlation can be achieved if the mixed liquid volatile suspended solids concentration is used.
- Dissolved surfactants have no significant impact on the oxygen transfer in activated sludge. Instead, it seems that the impact on oxygen transfer by substances adsorbed to the floc surface increases, as sludge retention time decreases.
- The oxygen transfer coefficient increases and the α-factor decreases with increasing airflow. Consequently, the oxygen transfer efficiency decreases. This phenomenon is especially pronounced at high oxygen transfer coefficients and high floc volumes.
- The reactor designs (airlift, bubble column) tested in this study have no verifiable effect on the α-factor.
- A combination of the experimental results shows that, for a constant floc volume, the α-factor improves with increasing sludge retention time, while it decreases with increasing floc volume for constant sludge retention times.

Based upon currently available data, the consequences for practice are:

- The increase in α-factor compensates the increase in oxygen uptake rate by the bacteria with increasing sludge retention time. Consequently, the required standard oxygen transfer rate decreases with increasing sludge retention time if the floc volume remains constant.
- Adapting the sludge retention time during the summer to the minimum required (temperature adjusted) does not lead to a significant reduction in the required standard oxygen transfer rate.

Kurzfassung

Die vorliegende Dissertation analysiert den Einfluss von Belebtschlamm auf den Sauerstoffübergang im Belebtschlammverfahren. Dies beinhaltet auch die Untersuchung der Wirkung oberflächenaktiver Substanzen im adaptierten Belebtschlammgemisch. Hierzu wurden Versuche mit synthetischem Grauwasser und realem Abwasser bei jeweils unterschiedlichen Schlammaltern in unterschiedlichen Versuchsanlagen durchgeführt. Weiterhin wurde eine Methode entwickelt, die in der Lage zu sein scheint, den volumetrischen Feststoffgehalt (Flockenvolumen) in Belebtschlämmen zu bestimmen. Die wesentlichen Ergebnisse können wie folgt zusammengefasst werden:

- Das Flockenvolumen beeinflusst wesentlich den Stoffübergang und die Sedimentationseigenschaften in bzw. von Belebtschlamm. Mit steigendem Flockenvolumen wird der Stoffübergang in die flüssige Phase verringert sowie das Absetzen der Flocken behindert. Der Effekt des Flockenvolumens beeinflusst den Stoffübergang von grobblasigen sowie feinblasigen Belüftungssystemen in gleicher Weise. Damit unterscheidet sich dieses Phänomen wesentlich von dem Einfluss oberflächenaktiver Substanzen auf den Stoffübergang.
- Der Trockensubstanzgehalt eignet sich nicht zum Vergleich von Phänomenen, bei denen das Flockenvolumen eine Rolle spielt. Eine bessere Korrelation der unterschiedlichen Ergebnisse gelingt unter Verwendung des organischen Trockensubstanzgehalts.
- Echt gelöste oberflächenaktive Substanzen haben kaum einen Einfluss auf den Stoffübergang in Belebtschlamm. Stattdessen zeigt sich, dass der Einfluss von an der Schlammflocke adsorbierten Substanzen mit sinkendem Schlammalter steigt und den Sauerstoffeintrag erniedrigt.
- Mit steigendem Luftvolumenstrom steigt der Stoffübergangskoeffizient an, allerdings sinkt der α-Wert. Folglich verringert sich die Effizienz des Eintrages. Dieses Phänomen ist bei hohen Stoffübergangskoeffizienten und Feststoffgehalten besonders ausgeprägt.
- Bezüglich der unterschiedlichen Reaktorkonfigurationen konnte kein Einfluss auf den α-Wert abgeleitet werden.
- Eine Zusammenführung der verschiedenen Ergebnisse ergibt, dass bei konstantem Flockenvolumen mit steigendem Schlammalter der Stoffübergang verbessert wird, während bei konstantem Schlammalter und steigendem Flockenvolumen dieser sich verschlechtert.

Die Konsequenzen dieser Erkenntnisse für die Praxis auf Basis der zur Verfügung stehenden Daten sind folgende:

- Der Anstieg des α-Wertes überkompensiert den Anstieg der Zellatmung mit steigendem Schlammalter. Dadurch sinkt die notwendige Sauerstoffzufuhr mit steigendem Schlammalter bei ansonsten konstanten Bedingungen.
- Eine Anpassung an das Mindestschlammalter im Sommer durch Herabsetzen des Trockensubstanzgehaltes führt zu keiner signifikanten Verringerung der notwendigen Sauerstoffzufuhr.

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My first acquaintance with scientific work occurred in Santiago de Compostela, Spain, at the department of Environmental Engineering and Bioprocesses, during my *Diplomarbeit*. Without the positive experience there, I probably would not have chosen the *Institut IWAR*. Thanks to Anuska, Luis, Marta, Gemma, Fernando, Belen, Ana, Elena, Carmen, Gonzalo, Almudena. I hope we will meet again somewhere, somehow.

All beginnings are difficult and my start at the Institut IWAR was certainly more difficult than anything I had done previously, including living in Russia without knowing Russian. I was taken off the first project because of my talent to call things by their names, which was very non-pc. Shame on me! Afterwards I developed a research project that did not find the right supporter and is now being realized somewhere in India. Finally, I ended up in the Megaproject "Semicentralized Supply and Treatment Systems for Urban Areas in China", with my colleagues Yue and Alessandro being responsible for the construction and operation of two pilot-scale membrane bioreactors for treating synthetic wastewater. It took more than one year till the whole facility was built up, not to mention the additional time before we got our first results. But we did it! Thank you, Yue, for taking over all that bureaucratic work and for the awesome smell of dried fish from China. Thank you, Alessandro, for showing me how to prepare "Zabaglione", the Bud Spencer songs after lunch and for reflecting many times on the basics of wastewater engineering: Viva la evolution!

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Finally the greatest thanks to my girlfriend Isolda – I hope it was worth all that suffering, to my parents who let me go my way, and my brother – I know you had a hard time being my brother – I love you all.

Jochen

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Notation

A	m²	surface area
a	m²/m³	interfacial area
A_B	m²	bubble surface
A_G	m²	total gas surface
ATV		Abwassertechnische Vereinigung
BOD	mg/L	biochemical oxygen demand
C	-	capita
c	mol/L	bulk concentration
c_0	mg/L	concentration at time zero
$c_{BOD,in}$	mg/L	*BOD* concentration in the influent
c_d	-	drag coefficient
c_i	mol/L	interface concentration
c^*_L	mol/L	liquid interface concentration
c'_L	mg/L	saturation concentration under process conditions
$c_{SS,in}$	mg/L	suspended solids concentration in the influent
$c_{\infty,CW}$	mg/L	oxygen saturation concentration in clean water
$c_{\infty,WW}$	mg/L	oxygen saturation concentration in wastewater
COD	mg/L	chemical oxygen demand
CST	s	capillary suction time
D	m²/s	diffusion coefficient
d_O	m	orifice diameter
d_B	m	bubble diameter
DNA		deoxyribonucleic acid
DOC	mg/L	dissolved organic carbon
DVWK		Deutscher Verband für Wasserwirtschaft und Kulturbau
Eo	-	Eötvös number
EPA		US environmental protection agency
EPS		extracellular polymeric substance
F/M ratio		food to mass ratio
g	m/s²	gravitational acceleration

GC-MS		gas chromatography - mass spectrometry
HFV	mL/L	hydrostatic floc volume
j	mol/(m²·s)	mass flux
k	L/(m²·s)	proportional constant
k_B	kg·m²/(s²·K)	Boltzmann's constant
k_L	m/s	liquid film coefficient
k_La	1/h	oxygen transfer coefficient
K_{ow}	-	water octanol partition coefficient
L_{BOD}	kg/d	*BOD* load
$MLISS$	g/L	mixed liquid inorganic suspended solids
$MLSS$	g/L	mixed liquid suspended solids
$MLVSS$	g/L	mixed liquid volatile suspended solids
M_{SS}	kg	mass of sludge (suspended solids)
Mo	-	Morton number
N	mol	number of molecules
OUR	kg O_2/d	oxygen uptake rate by the microorganisms
OSR	kg O_2/d	oxygen saving rate
OTR_{field}	kg O_2/d	oxygen transfer rate required under process conditions
PAC		powdered activated carbon
Q	m³/h	flow
r	mol/(L·s)	reaction term
r_{O_2}	m	diameter of oxygen molecule
Re_B	-	Reynolds number of the bubble
r_{resp}	mol/(L·s)	respiration rate of microorganisms
r_{fb}	m	radius of the force-balance bubble
SDS		sodium dodecyl sulfate
Se	-	surface coverage ratio
SGV	m³/(m²·h)	superficial gas velocity
$SOTR$	kg O_2/d	standard oxygen transfer rate
SRT	d	sludge retention time
SVI	mL/g	sludge volume index

T	°C	temperature
t	s	time
t_p	s	oxygen probe response time
t_f	s	characteristic time of mass transfer
V_B	m³	bubble volume
V_F	m³	final bubble volume
V_{fb}	m³	force balance bubble volume
V_L	m³	liquid volume
V_R	m³	reactor volume
w_B	m/s	bubble rise velocity
$w_{B,rel}$	m/s	relative bubble rise velocity
w_L	m/s	liquid flow velocity
y_e	-	molar fraction of oxygen in the inlet gas
y_s	-	molar fraction of oxygen in the offgas

Greek symbols

α		wastewater correction factor for oxygen transfer coefficient
β		wastewater correction factor for oxygen saturation
δ	m	film thickness
ε_L	-	liquid holdup
ε_P	-	particle holdup
η	kg/(m·s)	dynamic viscosity
θ	-	temperature correction factor
ρ_O	kg/m³	oxygen density
ρ_L	kg/m³	liquid density
ρ_G	kg/m³	gas density
σ	N/m	surface tension
τ_W	Pa	shear stress
φ	degrees	contact angle
Ω	-	pressure correction factor

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1 Preface

All Life is Problem Solving - Alles Leben ist Problemlösen

Knowledge does not start from perceptions or observations or the collection of data or facts; it starts, rather, from problems. One might say: No knowledge without problems; but also, no problems without knowledge. But this means that knowledge starts from the tension between knowledge and ignorance:
No problems without knowledge – no problems without ignorance.
For every problem arises from the discovery that there is something amiss within our supposed knowledge; or, viewed logically, from the discovery of an inner contradiction in our supposed knowledge, or of a contradiction between our supposed knowledge and the facts; or, to be more accurate, from the discovery of an apparent contradiction between our supposed knowledge and the supposed facts.

Die Erkenntnis beginnt nicht mit Wahrnehmungen oder Beobachtungen oder der Sammlung von Daten oder von Tatsachen, sondern sie beginnt mit Problemen. Kein Wissen ohne Probleme – aber auch kein Problem ohne Wissen. Das heißt, dass sie mit der Spannung zwischen Wissen und Nichtwissen beginnt:
Kein Problem ohne Wissen – kein Problem ohne Nichtwissen.
Denn jedes Problem entsteht durch die Entdeckung, dass etwas in unserem vermeintlichen Wissen nicht in Ordnung ist; oder logisch betrachtet, in der Entdeckung eines inneren Widerspruches in unserem vermeintlichen Wissen, oder eines Widerspruches zwischen unserem vermeintlichen Wissen und den Tatsachen; oder vielleicht noch etwas richtiger ausgedrückt, in der Entdeckung eines anscheinenden Widerspruches zwischen unserem vermeintlichen Wissen und den vermeintlichen Tatsachen.

Karl Popper 1962: Die Logik der Sozialwissenschaften, in: Theodor W. Adorno u.a.: Der Positivismusstreit in der deutschen Soziologie, Darmstadt, S. 103

2 Introduction

"Oxygen means money!" The relevance of oxygen transfer in activated sludge processes cannot be expressed more succinctly. Indeed, oxygen supply is still the largest energy consumer in the activated sludge process (~ 60 %, Roth (1998)), although the most important breakthroughs, e.g. the automation of oxygen control and the change from coarse bubble aeration to fine bubble aeration systems to cover the biological oxygen demand in conventional activated sludge plants, occurred in the early 1980s and have since been put into practice.

The selection of an appropriate α-factor, i.e. the relationship of wastewater to clean water oxygen transfer coefficient, plays an important role in estimating the required standard oxygen transfer rate (*SOTR*, see Appendix, Section 11.1, page 117), which is the key parameter in diffused aeration systems.

$$\alpha - factor = \frac{k_L a_{wastew.}}{k_L a_{cleanw.}} \qquad (2\text{-}1)$$

with

$k_L a_{wastew.}$	[1/h]	oxygen transfer coefficient in wastewater
$k_L a_{cleanw.}$	[1/h]	oxygen transfer coefficient in clean water

A factor sensitivity analysis reveals that the α-factor has the greatest impact on the calculation of the required *SOTR*. While other parameters that influence *SOTR*, such as temperature, the biochemical oxygen demand load (*BOD* load), oxygen saturation concentration, etc., can be estimated before the design of a wastewater treatment plant, approximation of the corresponding α-factor, based on the wide spread of its value in literature and its manifold dependencies, is difficult.

Generally, oxygen transfer in municipal wastewater treatment plants is lower than in clean water. Consequently, the α-factor is between 0 and 1. Some observations collected to date about what influences the α-factor in activated sludge can be summarized as follows:

1. With increasing mixed liquid suspended solids concentration (*MLSS* concentration), the α-factor declines. Most recent studies reported an exponential decrease (Günder (1999), Rosenberger (2003), Krampe and Krauth (2003), Krause (2005), Germain et al. (2007)), which is ascribed to the oxygen transfer inhibition effect of increased viscosity.
2. With increasing sludge retention time (*SRT*), the α-factor is enhanced. This phenomenon is ascribed to substances present in the liquid phase, namely dissolved surfactants, which negatively affect the α-factor and are better degraded with increasing *SRT* (EPA (1989), Gillot and Heduit (2008), Rosso et al. (2008)).
3. In plug flow systems, the α-factor is lowest for the influent and increases to a maximum for the effluent. In this case, better degradation of the substances that negatively affect the α-factor with increasing residence time is assumed (Kayser (1967), EPA (1989)).
4. Coarse bubble aeration systems have higher α-factors than fine bubble systems. Because of the higher surface renewal rate of coarse bubbles compared to fine bubbles,

the accumulation of surfactants that negatively affect oxygen transfer (Gilbert (1979), Rosso et al. (2008)) at the bubble interface can be offset.

5. Wastewater characteristics that change with time of day or day of the week lead to the large variety of α-factors observed in the same treatment plant (Gilbert (1979)).

6. Besides the wastewater characteristics, biological factors, such as the production of extracellular polymeric substance (EPS), DNA content and changes in metabolism, may also affect the α-factor (Steinmetz (1996))

The first two sets of observations seem inconsistent, because the *SRT* in wastewater treatment plants can be increased by raising the *MLSS* concentration. According to the first set of observations, this should lead to a decrease in the oxygen transfer coefficient; according to the second set, an increase. Currently no consolidation of these two observations exists. Additionally, investigations that try to correlate the α-factor to impact factors, such as *SRT*, *MLSS* concentration, *F/M* ratio, viscosity and diffuser airflow rate in real wastewater plants, show deviations of 30 % and higher (Krampe and Krauth (2003), Krause (2005), Germain et al. (2007), Rosso et al. (2008), Gillot and Heduit (2008)). Last but not least, the studies which investigated the effect of surfactants on oxygen transfer were limited to two-phase systems (gas /liquid) or non-adapted phase systems.

This limited knowledge about one of the most important parameters for the design of activated sludge plants was the motivation for this work. Its objectives are:

1. To provide deeper insight into the liquid/air/solid interactions in activated sludge and to attempt to explain the inconsistent observations of other studies.

2. To rectify the impact of surfactants, viscosity and *MLSS* concentration on oxygen transfer in activated sludge.

3. To demonstrate the implications that the new observations may have in practice.

Outline and structure of this thesis

Since aerated activated sludge is a three-phase system consisting of liquid, solid and gas phases, any prediction of the gas transfer in such a system implies that the influence of the other two phases on the gas transfer are well understood. Therefore, in Chapter 3, “Theory and Background”, the principles of oxygen transfer in three-phase systems are explained in detail. This includes a description of the properties of the phases in the process, namely air, water, and sludge, and their possible interactions. Finally, experience with activated sludge in wastewater engineering is summarized. The focus is on submerged aeration systems, with a detailed examination of the differences between fine bubble and coarse bubble aeration systems, because they are widely applied in wastewater engineering.

“Materials and Methods” are introduced in Chapter 4. In Chapter 5, the results of the experiments are presented and discussed in five sections. Each section builds upon the results of the previous one:

- Section 5.1, “Greywater Experiments Part I”, investigates the impact of *MLSS* and high surfactants concentrations on adapted sludge from two membrane bioreactors equipped

with coarse bubble and fine bubble diffuser types. Synthetic greywater is used for these studies. The systems operate at elevated *SRT* (> 20 d).

- In Section 5.2, “Greywater Experiments Part II”, the experiments of Part I are repeated and extended to include *SRT* lower than 20 d. The interaction between the *SRT* and the organic fraction is investigated. Experiments with iron hydroxide are examined to study the effect of biologically non-active, floc-like substances. A method is developed to determine the floc volume to enable a comparison of the results.
- In Section 5.3, “Wastewater Experiments”, the investigations on greywater sludge are extended to include municipal wastewater. The lowest *SRT* tested is 2 d. The results are discussed and compared to those in previous chapters. To obtain a better insight into the adsorption and floc volume effect, experiments with activated sludge and powdered activated carbon in a separate column are performed. The experiments with iron hydroxide are expanded to coarse bubble aeration systems and compared to the results of diluted activated sludge equipped with fine bubble aeration.
- Section 5.4, “Oxygen Transfer Phenomena - new insights”, uses the results to explain the various interactions between the solid, liquid and gas phases relevant to wastewater sludge.
- In Section 5.5, the consequences of the new findings are compared to current procedures and experience in practice.

Finally, the results are summarized in Chapter 6 and an outlook for future research is given in Chapter 7.

3 Theory and Background

Oxygen transfer into activated sludge is a very challenging issue in the field of multiphase flows. It presumes knowledge of biological, chemical, physical and hydrodynamic processes. Beside the physical mass transfer phenomena between the gas, liquid and solid phases, the transport mechanisms are overlapped by time and temperature-varying microbiological activity, impurity loads, desorption and adsorption processes.

The following pages present the current knowledge of mass transfer mechanisms, bubble formation and rising phenomena, and summarize experiences of fluid dynamics for three phase systems. The examples hark back to investigations in chemical engineering. Wherever possible, the topic will be narrowed down to the relevant application range in wastewater engineering, with the focus being on submerged aeration systems.

Chapter 3.1 introduces the basic properties of the phases involved that affect oxygen transfer in activated sludge or are required later to explain certain phenomena.

3.1 Air, oxygen, water and sludge

Air consists of 20.9 % oxygen (O_2) and 78 % molecular nitrogen (N_2), the rest is trace gases, for example, carbon dioxide (CO_2, 0.039 %). Air's major components, nitrogen and oxygen, are nonpolar molecules and therefore an uncontaminated air-water interface, for example when bubbles are released into water, is a strongly hydrophobic surface (see Craig (2004)).

In contrast, water (H_2O) is a polar liquid, where hydrogen atoms are covalently bonded to oxygen in a water molecule and have an additional attraction to the nearest oxygen atom of a separate water molecule. These hydrogen bonds between water molecules hold them closer than would be expected in a simple liquid with just Van der Waals forces, and change it to an anomalous liquid (high heat capacity, expansion on freezing, maximum density at 4 – 7 °C, high dielectric constant). Unlike 'simple' liquids, water's molecular structure is dominated not by the strong repulsions between molecules but by the directional, attractive interactions of hydrogen bonds (Ball (2004)). Water is a Newton fluid and consequently its viscosity is independent of the shear rate applied.

Since nitrogen gas and oxygen gas are nonpolar molecules, both poorly dissolve in water (polar), while carbon dioxide (CO_2), which is polar, dissolves more easily. Their saturation concentration in water at a temperature of 20°C and 1013 hPa air pressure using pure gases is around 18 mg/L for nitrogen, 46 mg/L for oxygen and 1716 mg/L for carbon dioxide, not considering the pH dependant reaction of carbon dioxide in water. However, in air the concentration of carbon dioxide is very low and consequently the saturation concentration in water at the conditions mentioned above is only about 0.7 mg/L while for oxygen and nitrogen it is around 9 mg/L and 14 mg/L, respectively.

Activated sludge primarily consists of flocs surrounded by a liquid. The floc is formed through a process of complex organization of heterogeneous materials, such as bacteria, macromolecules and inorganic material (Andreadakis (1993)). Generally, the bacterial cell fraction contributes only 5 – 20 % of the organic matter in the floc. More than 50 % can be attributed to extracellular polymeric substances (EPS), which significantly determine floc

properties (Frolund et al. (1996), Wilen et al. (2003)). While most particles have a diameter smaller than 5 µm, the major part of the volume is flocs with a diameter higher than 140 µm and a specific volume greater than 130,000 µm³ up to 2,100,000 µm³ (Schmid et al. (2003)). An average density of 1.020 g/cm³ was found to be typical for activated sludge systems, which differs only slightly from that of water. The specific area of the floc ranges between 60 and 189 m²/(g dry sludge) (Andreadakis (1993)). The surface charge of the floc is mainly negative. As well as van der Waals attraction and electrostatic repulsion at the floc surface, hydrophobic and steric interactions are important in microbial floc formation (van Loosdrecht et al. (1987), Jorand et al. (1995), Fein et al. (1999), Hermansson (1999), Esparza-Soto and Westerhoff (2003)). Investigations performed by Jorand et al. (1998) indicate that EPS have both hydrophobic and hydrophilic properties and additional effects caused by lipid components are believed to determine floc-to-floc adhesion through hydrophobic interactions. Cell surface hydrophobicity (CSH) is considered an important factor for bacterial adhesion to the floc in wastewater. Zita and Hermansson (1997) and Olofsson et al. (1998) showed that bacteria with higher CSH easily attach to activated sludge flocs while bacteria with lower CSH remained mainly in the liquid phase. The fact that activated sludge flocs trap low water soluble organic compounds (Struijs et al. (1991)) supports the importance of hydrophobic forces at the floc surface. According to Liao et al. (2001), sludge at higher *SRT* (> 12 d) were significantly more hydrophobic than sludge at lower *SRT*s (< 9 d). Frolund et al. (1995) observed similar behavior.

The water fraction present in activated sludge can be categorized as “free” or bulk water and as “bound” water that is held within capillaries or on the particle surface by adsorption (Katsiris and Kouzelikatsiri (1987), Chu et al. (2005)). Besides water, the liquid phase consists of free moving bacteria, protozoa, dissolved (salts) and non-dissolved substances like colloids.

As well as the physicochemical and microbiological aspects of activated sludge, the rheological properties have been studied particularly intensively by several authors (Günder (1999), Krampe (2001), Rosenberger (2003), Krause (2005), Yang et al. (2009)). All conclude that activated sludge behaves like a non-Newtonian pseudoplastic fluid. Increasing shear stress leads to a decrease in viscosity and if the shear rate is kept constant for a certain period of time, viscosity reduces (viscoelastic). However, activated sludge is actually a suspension of a liquid/floc mixture. Therefore, the original definition of viscosity, which describes the resistance of a fluid, cannot be applied. As a consequence, the measured viscosity of sludge is called ‘apparent viscosity’.

3.2 Oxygen transfer into water – two phase phenomena

Mass transfer occurs whenever two phases that are not at physical equilibrium are brought into contact with each other. If air bubbles are released into pure water, all gases present in the air bubble will start moving from the gas to the liquid phase, driven by the Brownian motion, until they reach a state of equilibrium. The gas/liquid interface can be divided into a liquid interface, a gas interface and an interface surface (Figure 1). The models describing mass transfer (Film Theory, Penetration Theory) only differ in the mathematical formulation of the mass transfer through the interface surface.

3.2.1 Mass transfer in the two phase system water/air without chemical reaction

Generally, mass flux describes the number of molecules that pass a certain area at a certain time.

$$j = -\frac{1}{A} \cdot \frac{dN}{dt} \qquad (3\text{-}1)$$

with

j	[mol/(m²·s)]	Mass flux
N	[mol]	Number of molecules
A	[m²]	Area
t	[s]	Time

Assuming the liquid phase is completely mixed, mass transfer only occurs in a thin layer at the gas/liquid interface (any concentration gradient in the liquid phase is destroyed by turbulence). Generally, mass transfer is proportional to the difference between the bulk concentration and the interface concentration.

$$j = k \cdot (c_i - c) \qquad (3\text{-}2)$$

with

k	[L/(m²·s)]	Proportional constant
c	[mol/L]	Bulk concentration
c_i	[mol/L]	Interface concentration

Under the assumptions that boundary effects can be neglected, neither sources nor sinks are present in the system, the solubility of the exchanging components is low (application of Henry law is valid) and that mass transfer mainly depends on the resistance of the liquid interface, Equation 3-3 can be developed by dividing the mass flux j by the liquid volume and multiplying it by the total gas surface (Mueller et al. (2002)).

$$j \cdot \frac{A_G}{V_L} = k_L \cdot \frac{A_G}{V_L} \cdot \left(c_L^* - c\right) = k_L \cdot a \cdot \left(c_L^* - c\right) = \frac{dc(t)}{dt} \qquad (3\text{-}3)$$

with

A_G	[m²]	Total gas surface
V_L	[m³]	Liquid volume
c^*_L	[mol/L]	Liquid interface concentration
k_L	[m/s]	Liquid film coefficient
a	[m²/m³]	Interfacial area

Here c^*_L reflects the oxygen saturation concentration at the gas/water interface and $c(t)$ the actual concentration in the bulk of the liquid. $k_L \cdot a$ describes the oxygen transfer coefficient, where a is defined as A_G/V_L and describes the interfacial area, while k_L is the liquid film coefficient and describes the velocity of the transport. Experimental data have shown that the k_L value ranges in a relatively small range ($2 \cdot 10^{-3} \leq k_L \leq 5 \cdot 10^{-4}$ m/s) while the interfacial area a may range between ($10 \leq a \leq 10^4$ m²/m³) (Thiersch (2001)).

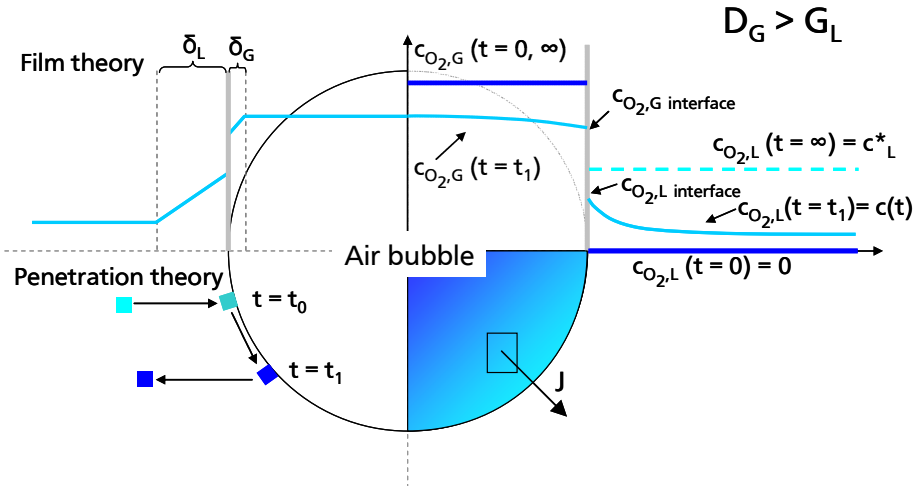


Figure 1: Concentration profile for oxygen mass transfer (right side: real; left side: model)

The interpretation of the film coefficient k_L depends on the diffusion model applied. For the stationary Film theory, k_L results in

$$k_L = \frac{D}{\delta_L} \qquad (3\text{-}4)$$

where

D	[m²/s]	Diffusion coefficient
δ	[m]	Film thickness.

However, mass transfer from rising bubbles in a water column is an instationary process. With the integration of Ficks second law for instationary one-dimensional diffusion

$$\frac{\partial c}{\partial t} = D \cdot \frac{\partial^2 c}{\partial x^2} \qquad (3\text{-}5)$$

and with the assumption of spherical bubbles, k_L for the penetration theory turns into

$$k_L = \sqrt{\left(\frac{D}{\pi \cdot t}\right)} \qquad (3\text{-}6)$$

where t represents the contact time of a fluid element at the interface (Figure 1, bottom left quarter). Higbie (1935) assumed the contact time to be the same for all fluid elements and arbitrarily assigned the constant contact time with the value of the ratio between bubble diameter d_B and rise velocity w_B of a bubble in a quiescent liquid ($w_B = w_{B,rel}$):

$$k_L = 2\sqrt{\left(\frac{D \cdot w_B}{\pi \cdot d_B}\right)} \qquad (3\text{-}7)$$

where

k_L	[m/s]	Liquid film coefficient
w_B	[m/s]	Bubble rise velocity
d_B	[m]	Bubble diameter

Experiments with single bubbles with a bubble diameter > 2 mm showed that the data are in good agreement with the theoretical value calculated with the Higbie model (Wagner (1991), Deckwer (1992)).

3.2.2 Single bubble phenomena: Bubble formation and bubble rise velocity

Air is fed into activated sludge systems mainly for two reasons: a) to provide the aerobic bacteria with sufficient oxygen; and b) to prevent the deposition of particles and the growth of a biofilm on the membrane surface, which reduces the permeate flow in membrane bioreactors. Mixing is a welcome side effect of aeration, however, if only mixing is required, mechanical agitation works more efficiently.

In the case of the first reason, commonly submerged fine bubble aeration systems are installed. These systems either have a slotted flexible membrane or are made of porous material with rigid orifices. Their task is to provide oxygen to the system as efficiently as possible. This is achieved by a high number of slits per surface area (up to 100,000 orifices/$m^2_{diffuser}$) with a small orifice diameter (d_O ~ 0.2 mm), a low specific air flow rate (< 0.15 cm^3_{Air}/(orifice·s)) which leads to bubble sizes smaller than 5 mm.

In the case of the second reason, a sufficiently high shear force (crossflow) is required. This is usually ensured with the installation of a coarse bubble aeration system. The system is characterized by a low number of holes (~ 100 orifices/$m^2_{diffuser}$), a relative big orifice diameter (d_O ~ 5 mm), a high specific air flow rate (~ 100 cm^3_{Air}/(orifice·s)) which leads to bubble sizes bigger than 20 mm.

The design and operating conditions of these diffuser systems significantly influence the bubble formation process and the bubble rise behavior at the orifice. The fundamental study of the bubble formation and bubble rising from single orifices is important for understanding which parameters influence these processes, for example, viscosity, density, surface tension, orifices size and airflow rate.

3.2.2.1 Bubble formation

Many authors estimated the bubble diameter or rather the bubble volume at single orifice using empirical models (Kumar and Kuloor (1970), Tsuge et al. (1997), Terasaka and Tsuge (2001), Martin et al. (2006)). The latest publications describe the bubble formation as a combination of simultaneous bubble expansion and rising. The expansion of the bubble can be approximated by the Rayleigh-Plesset equation, which includes inertial, capillary and viscous terms. The bubble rising while the bubble is still attached to the orifice is an overall balance of the forces acting on the bubble (Bals (2002); Yang et al. (2007)). A sketch and a table of the forces acting at the bubble can be found in the appendix (Section 11.3, page 119).

Buoyancy and surface tension forces determine bubble formation in fine bubble aeration systems (Loubiere and Hebrard (2003), Vafaei and Wen (2010)). An increase in surface tension leads to an increase in bubble volume and bubble detachment time (Gerlach et al. (2007)). In contrast, an increase in liquid density leads to lower bubble detachment times and a decrease in bubble volume (Gerlach et al. (2007)). In non-quiescent liquids, the liquid velocity (0.2 m/s) has a significant impact on bubble generation. With increasing liquid

velocity, bubble formation frequency increases and bubble sizes decreases (Loubiere et al. (2004)). The viscosity of the liquid has no impact on bubble formation as long as it is smaller than 100 times that of water (Gerlach et al. (2007)).

Buoyancy and the liquid inertia force control bubble formation in coarse bubble aeration systems (Kumar and Kuloor (1970)). The liquid inertia forces are so dominant that the liquid properties, such as viscosity, density and surface tension, have no significant effect on bubble formation (Kumar and Kuloor (1970)).

3.2.2.2 Bubble rise velocity

Once a bubble of a certain volume is released into the media, the bubble rise characteristics can be described in terms of the shape, rise velocity and motion of the bubble. These rise characteristics are closely related to the behavior of the bubble wake, and the flow and physical properties of the surrounding liquid. Besides the friction forces acting at the bubble head, the drag force is also influenced by the forces induced by the bubble wake. Although the role of the bubble wake on bubble rise velocity and mass transfer is now recognized (see Fan and Tsuchiya (1990)), detailed studies of the evolution of the flow in the wake and the forces acting on the bubble are extremely difficult. According to Brucker (1999), '*The strong lateral motion occurring beyond a critical size of the bubble results in the problem that the measuring probe cannot focus on a single location relative to the bubble. In addition, the wake structure of bubbles is basically three dimensional and unsteady, which again makes the measurement and interpretation problematic.'* However, the bubble wake characterizes a region of high sheer stress whose volume might be several times higher than the bubble volume (John et al. (2005)). Figure 2 portrays the bubble wake by measuring the concentration profile of oxygen in a fixed bubble (Paaschen (1998)).

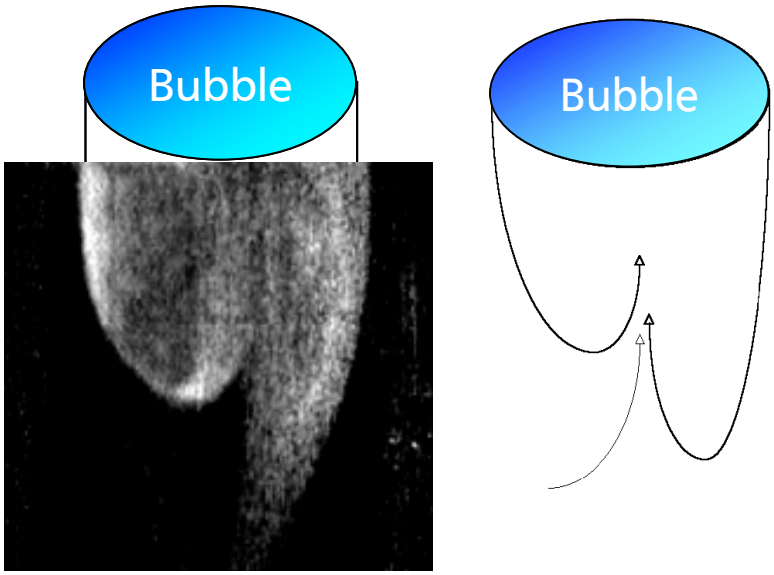


Figure 2: Bubble wake schematic. Left: The brighter the color, the higher the oxygen concentration in the wake. Right: Supposed flow regime (Paaschen (1998)).

The drag coefficient, which is required for the calculation of the drag force, incorporates friction and bubble wake forces. To approximate the drag coefficient, all calculations relate back to three dimensionless numbers:

1. The Reynolds number of the bubble (Re_B), which describes the relationship of inertia forces (first quotient) to friction forces (second quotient):

$$Re_B = \frac{w_B \cdot d_B \cdot \rho_L}{\eta_L} = \frac{w_B \cdot \rho_L \cdot V_B}{t} \cdot \frac{d_B}{\eta_L \cdot w_B \cdot A_B} \qquad (3\text{-}8)$$

where

w_B	[m/s]	Bubble rise velocity
d_B	[m]	Bubble diameter
ρ_L	[kg/m³]	Liquid density
η_L	[kg/(m·s)]	Dynamic viscosity
V_B	[m³]	Bubble volume
A_B	[m²]	Bubble area

2. The Eötvös number (Eo), which relates the effective buoyancy forces to the surface tension force (second quotient):

$$Eo = \frac{(\rho_L - \rho_G) \cdot g \cdot d_B^2}{\sigma} = (\rho_L - \rho_G) \cdot g \cdot V_B \cdot \frac{1}{\sigma \cdot d_B} \qquad (3\text{-}9)$$

with

ρ_G	[kg/m³]	Gas density
g	[m/s^2]	Gravitational acceleration
σ	[N/m]	Surface tension

3. The Morton number (Mo), which desribes the fluid properties:

$$Mo = \frac{g \cdot \eta_L^4 \cdot (\rho_L - \rho_G)}{\rho_L \cdot \sigma^3} \qquad (3\text{-}10)$$

With these three numbers, it is possible to estimate the bubble shape and the drag coefficient, which helps to approximate the bubble rise velocity (see Clift et al. (1978)).

Figure 3 introduces the single bubble rise velocity in water and liquids with different viscosities. The upper blue line in Figure 3 describes the bubble rise velocity in pure water; the area between upper and lower blue line represents the rise velocity for contaminated water. The green, orange, brown and black lines show the rise velocity in liquids with different viscosities (Tsuchiya et al. (1997)).

The colors of the bars at the top of Figure 3 correlate to the colors and numbers in Table 1 (red = 1; yellow = 2; violet = 3; light grey = 4; dark grey = 5); they describe the typical bubble shape and turbulence characteristics, expressed with the Reynolds number.

The relevant forces acting at the bubble and used in the text are introduced in the Appendix, Section 11.3, page 119.

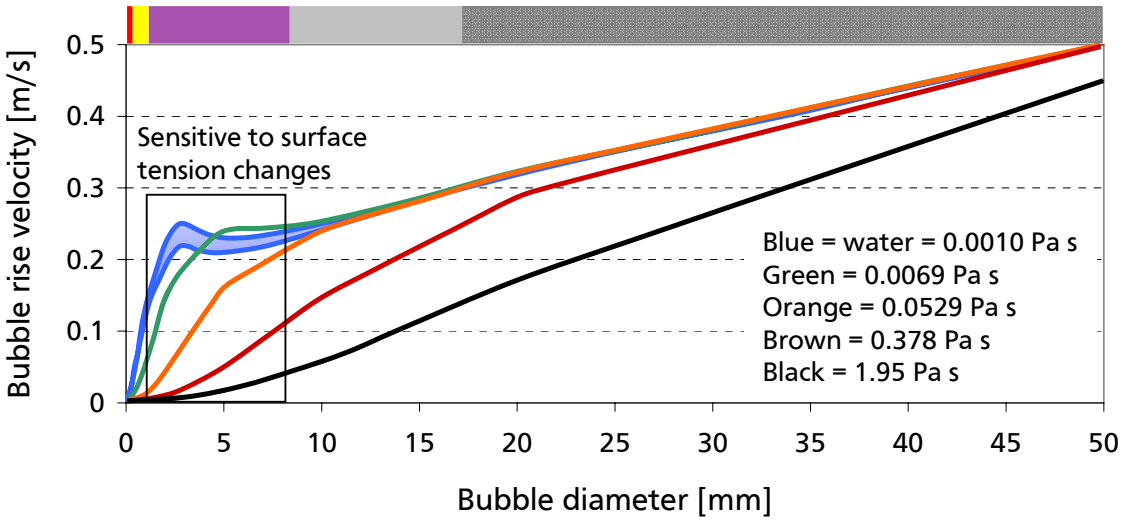
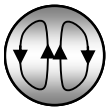
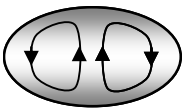
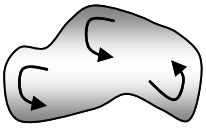
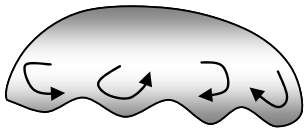


Figure 3: Single bubble rise velocity in pure water, contaminated water and for fluids with different viscosities (adapted from Tsuchiya et al. (1997))

Table 1: Characteristic bubble shapes, depending on the bubble diameters (adapted from Clift et al. (1978))

			Reynolds number	Bubble size
1	Spherical bubble with rigid interface		$Re_B < 1.4$	$d_B < 0.1$ mm
2	Spherical bubble with mobile interface		$1.4 < Re_B < 600$	$0.1 < d_B < 1.5$ mm
3	Ellipsoid bubble		$600 < Re_B < 1600$	$1.5 < d_B < 8.0$ mm
4	Irregular bubble		$1600 < Re_B < 4700$	$8.0 < d_B < 17$ mm
5	Shield bubble		$Re_B > 4700$	$d_B > 17$ mm

At small bubble sizes (red bar Figure 3, section 1 Table 1), mainly surface tension forces (F_σ) dominate. The bubble shape is spherical with a rigid interface and the bubble rises in a linear way. The bubble wake still shows laminar flow behavior.

For bubbles of intermediate size (yellow bar/section 2 and violet bar/section 3), the surface tension (F_σ) and drag forces (F_D) influence the shape and motion of the bubble. The shape changes from spherical to ellipsoid with a mobile interface and a typical zig-zag motion can be recognized. The bubble wake fades from laminar to turbulent flow behavior. In this range (0.1 mm < d_B < 8 mm), a change in surface tension and viscosity strongly affects the bubble rise behavior (Figure 3 black frame). These characteristics are typical for fine bubble aerations systems commonly installed to meet the biological oxygen demand in a wastewater plant.

For large bubbles (light grey bar/section 4 and dark grey bar/section 5), the liquid inertia forces (F_{IL}) start to dominate and surface tension and drag forces have less of an effect with increasing bubble size (Yang et al. (2007)). The rising of the bubble changes again to linear and the bubble wake flow stays turbulent. As in the case of bubble formation, changes in surface tension, liquid density and viscosity have only little to no effect on bubble rise behavior. These characteristics are typical for coarse bubble aeration systems as they are installed to create crossflow aeration in membrane bioreactors.

3.2.3 Bubble swarm phenomena

When air is supplied into a reactor by a diffuser many bubbles are released at the same time, which leads to the formation of a bubble swarm. This bubble swarm displays different behavior to a single bubble. Bubble unification (coalescence) and bubble breakup caused by bubble-bubble interaction change the single bubble properties. Additionally, the turbulence induced by a bubble's wake affects the rising of the following bubble and the liquid velocity. Therefore, the bubble characteristics in multipore systems differ by up to 20 % from the results observed at single orifices (Bals (2002)).

3.2.3.1 Bubble coalescence and bubble breakup

Bubble coalescence describes the unification of two single bubbles after a collision. However, not every bubble collision leads automatically to coalescence: it can also result in bouncing. Coalescence is often used as an explanation for the decrease in oxygen transfer observed in wastewater, though its mechanism is still not completely understood even for pure liquids (Craig (2004)). The bubble wake is the main driver of this interaction, since it triggers the probability of collision (Fan and Tsuchiya (1990)). If a bubble enters the rising column of liquid in another's wake under the right conditions, the two bubbles can contact and perhaps coalesce (Stewart (1995)). The result of a bubble-bubble collision depends on many effects, such as drainage time, the rate of adsorption and desorption of additives, the effects of surface tension gradients, hydrodynamic interactions, and nanohydrodynamic attractive and repulsive forces, such as van der Waals and hydration forces (Tsang et al. (2004)).

If two bubbles contact each other, the repulsive force between the interfaces must overcome the Laplace pressure ($2\sigma/r$) associated with the surface tension of the bubbles. Since "r" is the bubble radius [m] and σ the interfacial tension [N/m], it should be expected that the required repulsive force must be larger for fine bubbles than for coarse bubbles. However, Lehr et al. (2002) observed that bubbles only coalesce if the relative velocity of approach, vertical to the

surface of contact, was lower than a given value, the so-called ‘critical velocity’(Ribeiro and Mewes (2007)). The critical velocity for bubble coalescence did not depend on the bubble diameter but was a function of the physical properties of the liquid phase (Ribeiro and Mewes (2007)). In this context, the liquid temperature seems to enhance bubble coalescence (Ribeiro and Mewes (2006)).

Weiland and Bieker (1981) used a bubble column and an airlift reactor to demonstrate that liquid flow affects coalescence phenomena in phase systems. In a bubble column the liquid velocity is unsystematic/ chaotic, while in an airlift reactor the liquid flow can be divided into an upflow and downflow regime (Figure 4).

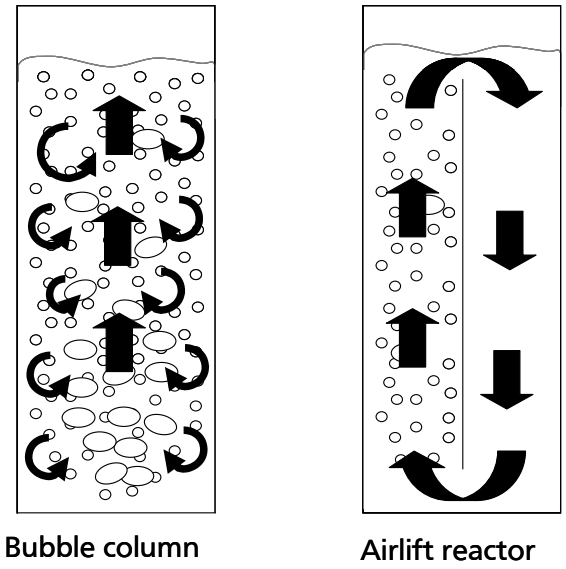


Figure 4: Schematic flow patterns in a bubble column and an airlift reactor

In the bubble column with increasing superficial gas velocity (0.5 – 1.5 cm/s), a clear increase in bubble size was observed. In the airlift reactor this coalescence phenomena was reduced with increasing upflow liquid velocity. At unrestricted circulation of the liquid in the airlift reactor the bubble size was almost independent of the superficial gas velocity and no coalescence phenomena could be observed. Consequently, at the same superficial gas velocity, airlift reactors are less affected by coalescence phenomena than bubble column reactors. This is of importance since in this dissertation a bubble column was used for the lab-scale experiments, while two pilot plants, one for greywater and the other for wastewater treatment, were designed as airlift reactors.

Bubble breakup only occurs in highly turbulent systems if the bubbles are bigger than a critical size. The bubble disintegrates if the available disruptive energy of the liquid can overcome the surface tension of the bubble (Lee et al. (1987)). This is typically the case in coarse bubble aeration systems since the Laplace pressure decreases with increasing bubble diameter. Experimental observations showed that bubble breakage occurs through the formation of a neck that closes two parts of the bubble. Here, the bubble wake of the preceding bubble plays an important role (Colella et al. (1999)).

3.2.3.2 Superficial gas velocity, flow regime and gas holdup

Many studies of aerated reactors have been performed to describe mass transfer phenomena. A comparison of the results is delicate since every research team has their own configuration. The publications often lack data for a valid comparison. A common parameter used to compare the air flow and oxygen transfer rates in different systems is the superficial gas velocity (*SGV* [$m^3_{air}/(m^2_{reactor\ surface\ area} \cdot h$]). It relates the airflow rate to the surface area of the reactor and should not be confounded with the bubble rise velocity. The *SGV* does not account for the number of orifice, the airflow rate through the orifice or the size of the orifice, which, as described before, all influence bubble characteristics. Thus, great care has to be taken when comparing results from different setups. In the field of wastewater engineering, two other important correlations are used: the specific air flow rate per reactor volume [$m^3_{air}/(m^3_{reactor\ volume} \cdot h)$] and per diffuser surface [$m^3_{air}/(m^2_{diffuser\ surface} \cdot h)$].

Typical parameters that are correlated with the *SGV* are the gas holdup and the flow regime. The gas holdup is one of the most important parameters as it characterizes the hydrodynamics and mass transfer in submerged aeration systems. On one hand, the gas holdup in a two phase system gives the volume fraction of the phases present in the reactor from which the residence time can be concluded. On the other hand, the gas holdup, together with the mean bubble diameter, determines the interfacial area. Since an exact calculation of the gas holdup based on mathematical models that use the properties of the diffuser and the reactor design is almost impossible, it is determined experimentally.

The flow regime generally depends on the quantity of air supplied to a system and the orifice diameter and therefore is closely related to the bubble formation process. The flow regime for fine bubble aeration systems can be differentiated into homogenous and heterogeneous regimes linked by a transition regime (Figure 5).

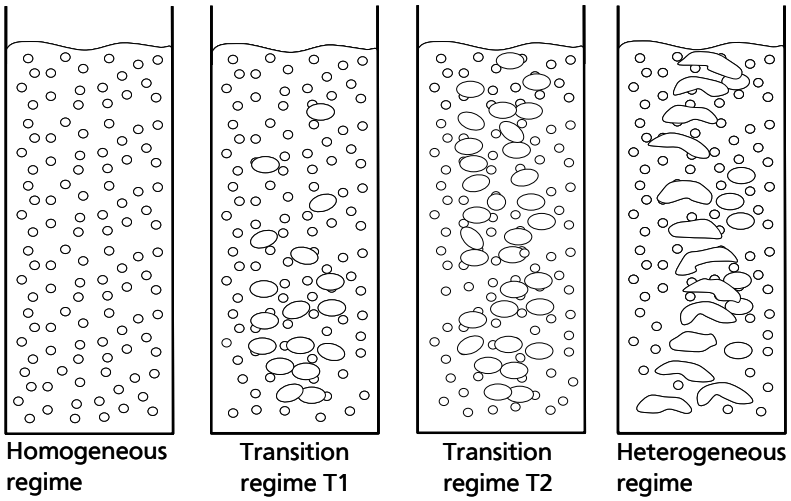


Figure 5: Flow regimes in bubble columns for fine bubble aeration systems (adapted from Shaikh and Al-Dahhan (2007))

Coarse bubble aeration systems already at low airflow rates cause a heterogeneous flow regime, which is then called the pure heterogeneous regime (Shaikh and Al-Dahhan (2007)).

Figure 6 demonstrates the difference between a pure heterogeneous flow regime (black points, coarse bubbles) and the shift of a homogeneous flow regime (white points, fine

bubbles) towards a heterogeneous flow regime both related to the gas holdup (Zahradnik and Kastanek (1979) and Zahradnik and Fialova (1996)).

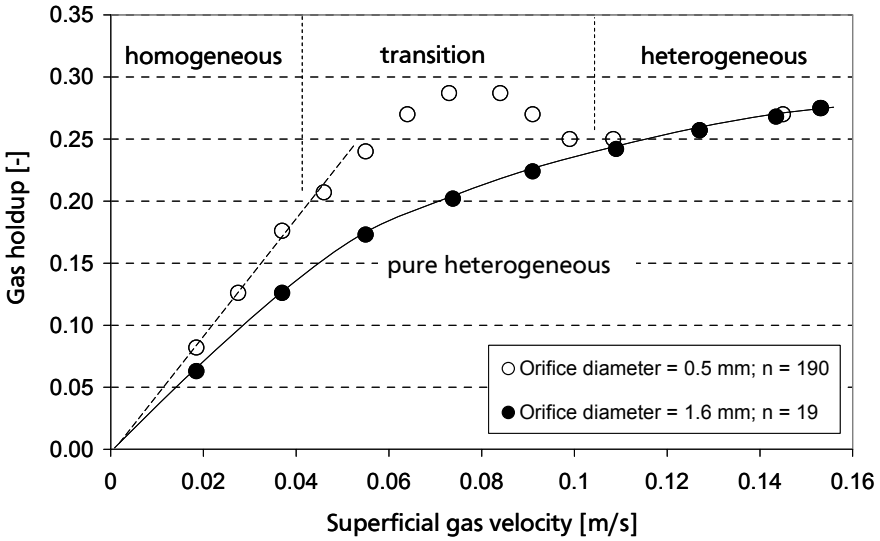


Figure 6: Gas holdup as a function of the superficial gas velocity for fine bubble systems (orifice diameter 0.5 mm) and coarse bubble aeration (orifice diameter 1.6 mm) (Zahradnik and Fialova (1996))

In the homogeneous flow regime the gas holdup (here 190 orifices, 0.5 mm diameter) first increases linearly with increasing *SGV*. The bubble size (d_B at *SGV* of 0.02 m/s ~ 4 mm) is the direct result of the nature of the distributor. The bubbles rise at an almost constant rate and the gas distribution over the reactor cross section is almost constant. According to Mena et al. (2005), coalescence is negligible and no large-scale liquid circulations occur in the bed. With increasing *SGV*, the flow regime enters the transition range, a mixture of homogenous and heterogeneous flow regimes, provoked by coalescence and increasing liquid circulations. The bubble size and shape distribution change, which leads to different rising velocities (Section 3.2.2.2). An approximation of the bubble volume, as introduced in Section 3.2.2.1, by the orifice diameter is no longer feasible. The gas holdup flattens then reaches a local maximum. A further increase in *SGV* leads to a decrease in the gas holdup. Finally, entering the heterogeneous flow regime the gas holdup increases again, showing similar values as the pure heterogeneous flow regime (black points). This regime is characterized by a wide bubble size distribution, due to the generation of large and highly non-uniform bubbles (Mena et al. (2005)). The gas holdup increases since coalescence as well as bubble break phenomena occur, which again increases the superficial area *a*.

In contrast to fine bubble aeration, the gas holdup in the pure heterogeneous system caused by coarse bubble aeration (19 orifices, 1.6 mm diameter, d_B at *SGV* of 0.02 m/s ~ 16 mm) increases steadily with increasing *SGV*. At low *SGV*, bubble coalescence and breakup accompany the process (Shaikh and Al-Dahhan (2007)).

The exact value for the transition point for fine bubble aeration systems depends on the reactor design (bubble column, airlift reactor, Jin and Lant (2004)) and the applied gas sparger (porous media, perforated plate, membrane diffuser; Hebrard et al. (1996)) but is usually in the range of 0.04 m/s for the two phase system water/air.

In wastewater engineering, the typically applied *SGV* to meet the biological oxygen demand with fine bubble aeration is around 0.0014 m/s (at 1 $m^3_{Air}/(m^3_{reactor\ volume} \cdot h)$ and 5 m reactor depth) and for membrane bioreactor systems usually equipped with coarse bubble aeration, 0.008 m/s (0.5 $m^3_{Air}/m^2_{Membrane\ surface}$). From this, it can be concluded that fine bubble aeration systems employed to meet the biological oxygen demand operate in the homogeneous flow regime. Coarse bubble systems, because of their bubble size (> 20 mm), always operate in the pure heterogeneous regime.

3.2.3.3 Rise velocity of a bubble swarm

In contrast to the single bubble introduced in Section 3.2.2.2, the bubble swarm induces a liquid velocity, which influences the rise velocity of the bubble. Figure 7 shows the relative bubble rise velocity depending on the gas holdup for a fine bubble aeration system (here d_B = 2 - 4 mm).

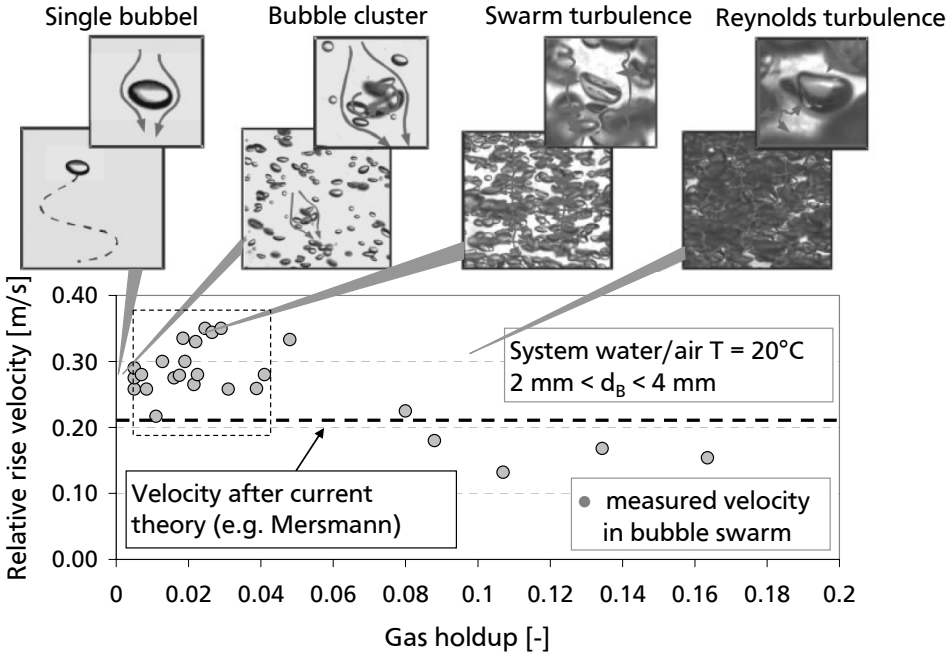


Figure 7: Relative rise velocity of a bubble swarm according to Schlüter (2002)

In contrast to the single bubble (Chapter 3.2.2.2), the bubble rise velocity in a bubble swarm is not constant at the same bubble diameter but depends on the gas holdup. Schlüter (2002) divides the bubble swarm velocity, depending on the gas holdup, into three segments:

a) At gas holdups below 0.005 the bubbles rise in a helical way with minimal interactions. Isolated bubble clusters occur, where a bubble enters the bubble wake region of another bubble, which leads to an increase in the bubble rise velocity.

b) With increasing gas holdup (0.005 – 0.048; dashed area) the bubble wake induced turbulence rises and the radial movement is reduced, which leads to a significant increase in the axial bubble rise velocity compared to the single bubble system.

c) With a further increase in gas holdup, the system enters the Reynolds turbulence region. In this region, the drag forces dominate the bubble rise behavior, which leads to a decrease in the bubble rise velocity.

Figure 8 depicts the impact of the gas holdup on the bubble wake structure. The bubble wake contracts with increasing gas holdup and the bubble-bubble interaction increases.

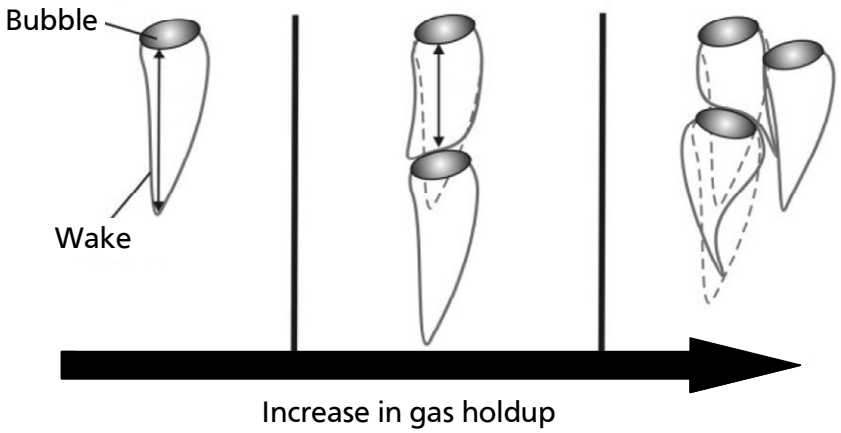


Figure 8: Impact of gas holdup on bubble wake (John et al. (2006))

The gas holdup applied in wastewater engineering using submerged aeration systems is in the range of 0.002 – 0.08 (Thiersch (2001)). Commonly, gas holdups higher than 0.05 are only achieved in membrane bioreactor systems with intensive coarse bubble aeration. Consequently, the fine bubble aeration systems used to meet the biological oxygen demand show flow patterns according to the swarm turbulence regime (Figure 7, dashed frame). In this region, the relative bubble rise velocity is higher than assumed for a single bubble, and the bubble wake is compressed by the influence of the preceding bubble.

3.2.4 The impact of electrolytes and organic surfactants

In the previous chapters, the bubble characteristics and behavior in clean water were introduced. In practice, the liquid phase also contains inorganic and organic substances that influence bubble behavior, for example, coalescence, bubble size, bubble rise velocity, diffusivity and consequently oxygen transfer. In this case, electrolytes and organic surfactants play a decisive role.

Generally, it is assumed that electrolytes increase surface tension, diminish bubble coalescence, and decrease the solubility of oxygen into water. The first assumption about surface tension is only partly true. Some electrolytes, like HCl, HNO_3 or $HClO_4$, decrease surface tension (Weissenborn and Pugh (1996), Appendix, Section 11.6, page 125). The order of this effect from increasing to decreasing follows the Hofmeister series, which was published in the 19th century (Hofmeister (1888)). But also the decrease in bubble coalescence after the addition of salts is not consistent. Craig et al. (1993) studied the effect salts on bubble coalescence (Table 2) and concluded that some salt combinations have an effect, some not.

Table 2: Effect of selected electrolyte combinations on the inhibition of bubble coalescence (+ = inhibition; 0 = no effect; Craig et al. (1993))

Cations / Anions	H^+	Li^+	Na^+	K^+	Cs^+	Mg^{2+}	Ca^{2+}	NH_4^+
OH^-	0		+	+				
Cl^-	0	+	+	+	+	+	+	
Br^-	0		+	+				
NO_3^-	0	+	+	+			+	
ClO_3^-			0					
ClO_4^-	+		0			0		0
CH_3COO^-	+		0	0	0	0		0
SO_4^-	0	+	+			+		
$(COO)_2^{2-}$	0			+				

In the last century, many theories tried to explain the mixed behavior of electrolytes, from "salting in, salting out", "hard and soft" to "hydrophobic and hydrophilic" effects, without success (Kunz (2006)). Hofmeister speculated that the effect is based on a change in water structure and that the interrelationship between the salt components with water and not with the interface is crucial. The problem was resolved only recently and involved a split from the current doctrine that states there are no atomic ions at the air/water interface of aqueous solutions (Garrett (2004)). Jungwirth and Tobias (2002) showed that if the accumulation of ions at the water/air interface caused by the ion-water interactions and the geometry of the water molecules at the interface is assumed, the experimental results concerning the effect of surface tension are consistent with the model predictions and the Hofmeister series. The importance of the polarizability of ions and their influence on the air/water interface is now recognized (Jungwirth and Winter (2008)), however, the potential impact of interfacial ions on bubble formation and coalescence behavior is only just beginning to be realized.

In one of the latest studies on coalescence behavior in bubble columns, Ruzicka et al. (2008) and Orvalho et al. (2009) observed that calcium chloride ($CaCl_2$), sodium sulfate (Na_2SO_4) and sodium chloride (NaCl) had a dual effect on the gas holdup. In the homogeneous flow regime (here $SGV < 0.03$ m/s) the addition of salts had almost no effect. In the transition regime ($SGV > 0.03$ m/s) with increasing salt concentration up to a concentration of 0.1 mol/L, the gas holdup increased in comparison to pure water, while at higher concentrations (> 0.1 mol/L) the gas holdup reduced again. The first behavior is well documented in the literature and can be accredited to the suppression of coalescence by a stabilization of the bubble/water interface. There is currently no explanation for the decrease in gas holdup with increasing salt concentration.

In municipal wastewater treatment, the concentration of electrolytes does usually not exceed 0.1 mol/L and most salts exist in the form of sodium, calcium, magnesium, potassium, chlorides, sulfates, carbonates and nitrates. If coalescence occurs, the increased concentration of salts in wastewater compared to clean water should lead to an increase in gas holdup,

which again increases the superficial area a and consequently the oxygen transfer coefficient $k_L a$.

Concerning the decrease in oxygen solubility with increasing salt concentration, all tested electrolytes decrease oxygen solubility in water (Weissenborn and Pugh (1996), see Appendix, Section 11.6, page 126). It is assumed that the hydration of the electrolytes reduces the activity of water and the space available for the solution of gas molecules. Consequently, the solubility of oxygen decreases. This effect is considered in wastewater engineering by the introduction of the salt correction factor (β-factor), which is defined as the ratio of the oxygen saturation concentration in wastewater to clean water (Gilbert (1979)):

$$\beta - factor = \frac{c^*_{\infty;WW}}{c^*_{\infty;CW}} \qquad (3\text{-}11)$$

with

$c^*_{\infty,WW}$	[mg/L]	Oxygen saturation concentration in wastewater
$c^*_{\infty,CW}$	[mg/L]	Oxygen saturation concentration in clean water

In contrast to the unanswered questions on the interaction of electrolytes and the air/water interface, the mechanism of organic surfactants is relatively clear, as demonstrated by the number of publications (Eckenfelder and Barnhart (1961), Wagner and Pöpel (1996), Steinmetz (1996), Chern et al. (2001), Painmanakul et al. (2005), Rosso et al. (2006), Sardeing et al. (2006), Hebrard et al. (2009)).

According to Karsa (2006), '*Surfactants' (or 'surface active agents') are organic compounds with at least one lyophilic ('solvent-loving') group and one lyophobic ('solvent-fearing') group in the molecule. If the solvent in which the surfactant is to be used is water or an aqueous solution, then the respective terms 'hydrophilic' and 'hydrophobic' are used'*. The head is usually a functional group (e.g. alcohol, carboxylic acid, etc.) and the tail involves aliphatic chains. Organic surfactants are attracted to the hydrophobic gas-liquid interface where they adsorb and lower the surface tension very strongly (Figure 9). Exemplary sodium dodecyl sulfate (SDS, sodium lauryl sulfate, $C_{12}H_{25}NaO_4S$), one of the most common surfactants for fabrication of soaps, detergents and emulsifying agents and thus frequently present in wastewaters (Hebrard et al. (2009)), is pictured in Figure 9.

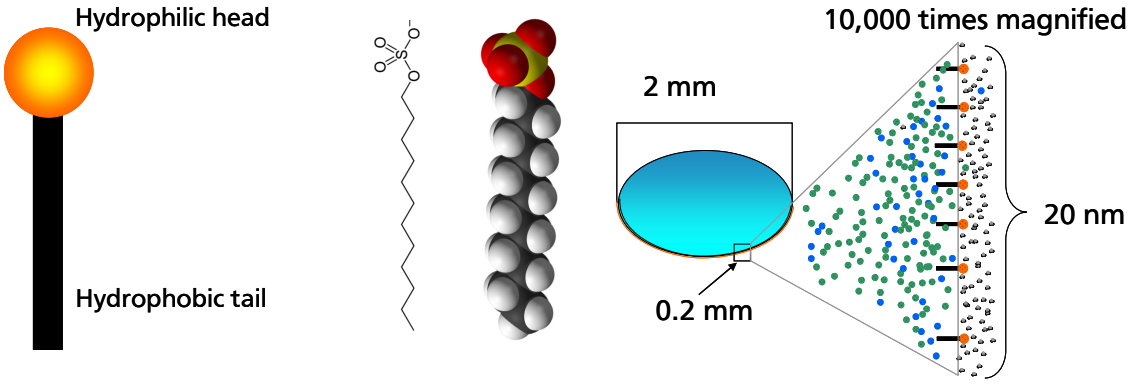


Figure 9: Left: sketch of an organic surfactant; middle: Chemical structure of SDS (Source: Wikipedia (2010)); right: section of bubble water interface loaded with surfactant

Above a critical molecule concentration, the critical micelle concentration (cmc, for SDS ~ 2.4 g/L), surfactants spontaneously form micelles (Figure 10). These micelles are commonly in the range of several nanometers (~ 5 nm), with their polar part orientated to the polar water phase (Bales et al. (1998)).

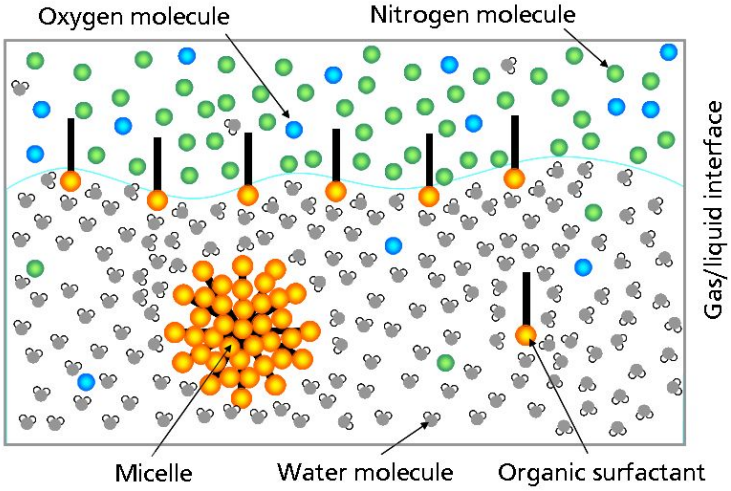


Figure 10: Organic surfactant properties at the liquid/gas interface

Sodium dodecyl sulfate was used in numerous experiments to study the impact of surfactants on oxygen transfer in clean water (Gillot et al. (2000), Painmanakul et al. (2005), Rosso et al. (2006), Chen et al. (2007)). All studies concluded that this surfactant has a negative effect on the overall oxygen transfer in water in the concentration range usually found in wastewater (10 – 100 mg/L).

The mechanism that permits organic surfactants to depress oxygen transfer in clean water is explained as follows:

a) With increasing surfactant concentration the surface tension is reduced, which leads to the formation of smaller bubbles (Appendix, Section 11.7, page 127). The maximum change in bubble size is observed when the maximum change in surface tension occurs. Since the bubble is capable of adsorbing organic surfactants, the critical micelle concentration is higher than in pure water and will be achieved after the bubble has reached its maximum adsorption rate (surface coverage ratio, Se). Beyond the critical micelle concentration, very little reduction in surface tension and therefore in the bubble diameter occurs. The decrease in bubble diameter produces two distinct results: an increase in the interfacial area, and a reduction in the terminal rise velocity (Section 3.2.2.2). Both lead to an increase in gas holdup.

b) Additionally, the accumulation of the surfactants on the superficies of the bubble leads to a reduction in the k_L value (Appendix, Section 11.7, page 129). Again, two effects need to be differentiated. On one hand, the diffusion coefficient is reduced due to the increased resistance at the bubble interface, caused by the adsorbed surfactants. On the other, the interface changes from mobile to more rigid, which lowers the surface renewal rate, reduces the turbulence of the bubble wake and consequently the coalescence tendency.

c) The overall effect on k_La is depicted in Figure 61 (Appendix, Section 11.7, page 129). With increasing surfactant concentration the k_La value is reduced until the maximum adsorption rate (Se = 1) of the bubble is achieved.

However, Kelkar et al. (1983), Ozturk et al. (1987) and Salvacion et al. (1995) observed that certain alcohol solutions that are also surface active substances have a positive effect on the k_La value and the gas holdup up to a certain carbon chain length (around 6 – 8). If the carbon chains were longer than 8, gas holdup and k_La were reduced. These observations demonstrate that hydrophobic attraction forces between the hydrophobic bubble interface and the hydrophobic carbon chains orientated to the bubble and the turbulence forces, caused by the bubble wake and the liquid flow, play a significant role in the overall effect of surfactants. High flow regime interfaces (e.g. coarse bubble aeration) are less affected by organic surfactant contamination and consequently show higher α-factors than low flow regime interfaces, as for example, fine bubble diffusers (Rosso et al. (2008)). If the attachment force of the surfactant can be removed through an increase in turbulence, an overall positive effect can be observed, as reported by Zlokarnik (1980) or Stenstrom and Gilbert (1981).

3.2.5 Influence of the diffuser type

In the past, little attention was paid to the influence of the diffuser type on bubble formation and bubble behavior, especially in the case of membrane diffusers as they are widely applied in wastewater treatment plants. Usually with an increasing airflow rate in coarse bubble aeration a slight increase in oxygen transfer efficiency is observed while for fine bubble aeration systems a decrease is reported (EPA (1989), Appendix, Section 11.8, page 130).

The behavior of coarse bubble aeration systems is explained by the bubble breakup that is caused by the high turbulence and air flow rate applied to these systems (Section 3.2.3.1) and the consequent increase in the superficial area with increasing airflow rate (Eckenfelder (1959)).

In the case of fine bubble aeration systems two designs have to be differentiated: porous disc diffusers and flexible membrane diffusers. Porous diffusers are characterized by a very narrow pitch assembly (< 1 mm). In this case, two or more orifices may contribute air to the formation of one bubble and the bubbles coalesce before it detaches (Kulkarni and Joshi (2005)). At low *SGV* an imperfect bubbly flow occurs, identified by a mixture of large and small bubbles (Hebrard et al. (1996)). The gas pressure drop stays constant with increasing *SGV* but the bubble size increases with increasing *SGV*. To exclude coalescence during bubble formation, the distance from one orifice to the other has to be the minimum diameter of the bubble size produced (critical inter-orifice distance, Bals (2002)). At sieve plates, it could be shown that the smallest bubbles are formed with the closest hole spacing of 6 mm (Kulkarni 2005). Since this is not the case in porous diffusers, coalescence always occurs in tap water (Kazakis et al. (2008)).

In contrast to porous diffusers, Hebrard et al. (1996) observed that flexible membrane disc diffusers produce perfect bubbly flow (homogeneous flow regime) up to gas holdups of 5 %, which corresponded to a superficial gas velocity of 0.02 m/s. The gas pressure drop and

bubble size increased with increasing *SGV*, which is caused by the higher airflow rate and expansion of the orifice (Loubiere and Hebrard (2003)).

Consequently, the similar decrease in oxygen transfer efficiency for porous diffusers (like ceramic disc and dome diffusers) and flexible membrane diffusers observed in practice is caused by different phenomena. In the former, unequally distributed bubble sizes is the product of very narrow distances of the orifice exceeding the critical inter-orifice distance, which enhances coalescence directly at the orifices. In the latter, the bigger bubble size is the consequence of bigger orifice diameter caused by the membrane stretching, which is greatly influenced by the aging of the membrane diffuser (Painmanakul et al. (2004)).

3.3 Oxygen transfer into three phase systems – the role of particles and sludge

So far, the effects relevant for understanding oxygen transfer in a two phase system have been described. If it is already challenging to measure the effects in a two-phase system (coalescence, bubble size, bubble rise velocity in a swarm), for three phase systems it is even more complicated, sometimes even impossible. Optical methods (high-speed camera) fail simply because of the opacity of sludge.

3.3.1 Mass transfer in three phase systems

The presence of a third phase requires the adoption of the mathematical model for a two phase system for the following reasons:

If the particles are inert and not porous and added to a two-phase system at a constant height they will displace some volume of the other two phases. Usually the addition of solids is expressed as a percent of the total volume observed without aeration (solid holdup). Because k_La expresses the volumetric mass transfer from the gaseous phase to the liquid phase, the volume of the solid phase that does not participate in oxygen transfer is excluded. According to Sun and Furusaki (1989), Equation 3-3 changes then into:

$$\frac{dc(t)}{dt} = \frac{k_L a}{\varepsilon_L} \cdot \left(c_L^* - c(t) \right) \qquad \text{and} \qquad \varepsilon_L + \varepsilon_P = 1 \qquad (3\text{-}12)$$

with

ε_L	[-]	Liquid holdup
ε_P	[-]	Particle holdup

If the particles are not inert but catalytic, Equation 3-12 changes into:

$$\frac{dc(t)}{dt} = \frac{k_L a}{\varepsilon_p} \cdot \left(c_L^* - c(t)_L \right) - r \qquad (3\text{-}13)$$

with

r	[mol/(L·s)]	Reaction term

If the particles are reactive and diffusive, as in the case of activated sludge, the volume fraction of the particles cannot be excluded from the overall mass transfer calculations, since oxygen diffuses into the flocs. However, up to now aerated activated sludge was not regarded

as a three phase system with gel-like, reactive particle properties because of the difficulty in determining the floc volume/particle holdup and its diffusivity. Consequently, all investigations concerning mass transfer in wastewater engineering used the following equation for mass transfer measurements:

$$\frac{dc(t)}{dt} = k_L a \cdot \left(c_L^* - c(t)_L\right) - r_{resp} \qquad (3\text{-}14)$$

with

r_{resp}	[mol/(L·s)]	Respiration rate
$k_L a$	[1/h]	Mass transfer coefficient in activated sludge, treated as a pseudo-homogeneous liquid

If the respiration rate is constant according to Kayser (1979), the equation changes to:

$$\frac{dc(t)}{dt} = k_L a \cdot \left(c_L^{'} - c(t)_L\right) \qquad (3\text{-}15)$$

with

$c_L^{'}$	[mg/L]	Oxygen saturation concentration under process conditions

Finally, if the tests are performed with an inflow or recirculation flow, Equation 3-15 changes into:

$$\frac{\partial c}{\partial t} = (k_L a + \frac{Q}{V_R}) \cdot \left(c_L^{'} - c(t)_L\right) \qquad (3\text{-}16)$$

with

Q	[m³/h]	Influent and recirculation flow
V_R	[m³]	Reactor volume

Sun and Furusaki (1989) showed that the diffusivity of gel-like particles additionally influences the result of oxygen transfer measurements and proposed an equation that considers this effect (Appendix, Section 11.9, page 131).

3.3.2 Impact of solids on mass transfer

Many studies have been performed to understand the impact of solids on the mass transfer in aerated reactors, especially in chemical engineering. Behling (2008) published a summary of the experimental work on three phase bubble columns.

Mena et al. (2005) summarizes eight ways how the gas-liquid system can be affected by solids. They are listed below with additional comments on their significance in submerged aeration systems in wastewater engineering.

Steric effect of solids: At the same gas holdup as in the two phase system, measured by the elevation of the volume in the reactor, the real gas holdup in a three phase system is increased by the factor 1/(1-solid holdup). A higher gas holdup at the same superficial gas velocity favors coalescence, which leads to a shift from the homogeneous flow system to the transition regime (Section 3.2.3). In wastewater engineering the solid (floc) holdup is a

parameter yet to be established. However, with increasing suspended solid concentration of the sludge (*MLSS*), the steric effect of the floc will increase.

Density of the suspension: With increasing density, the difference between the liquid and the solid phase and the apparent density of the mixture changes. This influences the hydrodynamic properties of the three-phase system. Since the sludge density is only slightly higher than the density of water (Chapter 3.1), little to no effect on mass transfer is expected.

Viscosity effect: With increasing viscosity, a reduction in the bubble rise speed may result in larger gas holdup at the same gas input. On the other hand, in viscous media, bigger and faster rising bubbles are formed, which results in lower gas holdup (Shaikh and Al-Dahhan (2007)). As explained in Chapter 3.2.2, viscosity in the common application range in wastewater treatment does not influence bubble formation and the bubble rise velocity is only reduced in the fine bubble aeration system. However the increase in apparent viscosity with increasing *MLSS* concentration decreases liquid velocity and lowers the gas holdup as measured by Jin et al. (2006). If this effect is caused by a bigger bubble formation provoked by lower liquid velocity (Loubiere et al. (2004)), or bubble coalescence affected by surface interactions between the bubble and the activated sludge floc, cannot be answered at the moment.

Physical chemistry of surfaces: Depending on the interfacial properties of the phase system (hydrophilicity/phobicity, wettability, etc.), particles tend to increase or reduce their concentration near the gas liquid interface. This interaction stabilizes the surface, which lowers the bubble rise speed and may affect the oscillation of the bubble shape. There are currently no investigations of the interaction between the activated sludge floc and the bubble surface regarding oxygen transfer available. However, as well as the stabilization of the surface, it is also conceivable that the superficial area *a* available for oxygen transfer or the contact time of a fluid element is influenced by this mechanism.

Bubble formation: With increasing solid concentration, additional downward forces exerted by settling solids on the growing bubble may increase the bubble size, which leads to a lower gas holdup. Again, this effect is conceivable for activated sludge, however, no investigations are currently available.

Bubble rise velocity in suspension: Generally, the influence of direct bubble–particle interactions reduces the bubble speed (Fan and Tsuchiya (1990); John et al. (2006)) by hydrodynamic forces and mutual collisions. Both effects delay the bubble motion and liquid velocity. This effect is very likely to occur in activated sludge and should lead to a higher gas holdup in the system, which again may favor bubble coalescence.

Bubble coalescence in suspension: The properties of the solids are very important here. Depending on the size, density and surface properties (wettability), solids can both suppress and promote coalescence. Although coalescence is often quoted as the reason for depressed oxygen transfer in activated sludge with increasing solid concentration, the microscopic effect is still unsolved.

Spatial inhomogeneity of solid particle concentration: The development of concentration profiles in the solid phase (not completely mixed reactor) may lead to a transformation of the

flow regime even if the bubbles are distributed uniformly. On the other hand, a statistically uniform distribution of solids can act against the clustering tendency of the gas phase and stabilize the bed. Generally, it is assumed that activated sludge is homogeneously distributed in the reactor. However, from hydrodynamic measurements in real wastewater treatment plants it is known that this is seldom the case in practice. How these inhomogeneities influence oxygen transfer in wastewater has not been studied yet.

Additionally, some investigations that replenish the above-mentioned mechanisms have been carried out (an incomplete list):

Van der Kroon (1968) investigated the effect of aluminum hydroxide flocs on oxygen transfer. A clear decrease in oxygen transfer can be observed with increasing solid concentration. At low concentration (< 1 g/L) the oxygen transfer rate was higher than in tap water (105 %) and became even more pronounced when the gas flow rate was decreased.

Deckwer and Schumpe (1983) described the effect of particles on the coalescence and breakup behavior. It is concluded that the final effect depends on the size ratio of the particles to the bubble and particle density. For small particles compared to the bubble with low density, a promotion of coalescence is reported. For bigger particles with high density, bubble breakup is observed. Since the size ratio of bubbles to activated sludge floc is around 20 (fine bubble) to 200 (coarse bubble) and the density of the activated sludge is around 1.020 g/cm³ (Andreadakis (1993)), it can be assumed that coalescence is promoted.

Andrews et al. (1984) discussed the impact of cell accumulation at the bubble interface. Cells landing by interception on a bubble rising through a fermentation broth are dragged around the interface by the fluid flow. They do not accumulate in the upper part of the bubble, where the majority of the oxygen transfer occurs. Consequently, neither chemical enhancement nor direct uptake can change the mass transfer rate. The cells accumulate near the rear stagnation point and, while chemical enhancement may become significant here, it will be counteracted by an interface blockage effect.

Sauer and Hempel (1987) investigated several materials for gas holdup and mass transfer in a bubble column with sintered and perforated orifices. In contrast to the gas holdup, where at small solid concentrations and low superficial gas velocity, higher values than in clean water could also be observed, the k_La always decreased when solid particles were added. It is concluded that the increase in interfacial area at enhanced gas holdups is compensated for by an even larger decrease in the liquid side mass transfer coefficient because of rapidly declining turbulences.

John et al. (2006) studied the impact of solid particles on the bubble rise behavior and concluded that particles can be incorporated into or excluded from the bubble wake, depending on their size. In all cases, it results in compression of the bubble wake, compared to the two-phase system (Appendix, Section 11.10, page 132), which lowers the turbulence in the system.

This section demonstrates the manifold interaction of solids in a phase system. Unfortunately, the results of oxygen transfer measurements in chemical engineering are usually not correlated with the α-factor. Usually the gas holdup or the oxygen transfer

coefficient k_La is compared with the superficial gas velocity and the solid holdup. This leads to a fundamental problem in wastewater engineering of how to identify the solid holdup, i.e. the floc holdup, of activated sludge. Up until now, sludge has been perceived as a pseudo-homogeneous medium and no method exists to determine the occupied volume of the activated sludge floc in the three-phase system.

3.3.3 Impact of activated sludge on oxygen transfer

To date, there have been two major sets of observations about the impact of activated sludge on oxygen transfer:

1. with increasing *MLSS* concentration the α-factor reduces
2. with increasing *SRT* the α-factor enhances

3.3.3.1 Impact of mixed liquid suspended solids concentration on oxygen transfer

Figure 11 demonstrates the results of authors who have studied the impact of the *MLSS* concentration on oxygen transfer without considering the effect of the *SRT*. The summarized data indicate that the α-factor decreases with increasing *MLSS* concentration quite linearly, although most authors imply an exponential function (Günder (1999), Krampe and Krauth (2003), Rosenberger (2003), Germain et al. (2007)). However, the values vary significantly, from 0.3 to 0.7, at a similar *MLSS* concentration (10 mg/L).

Two reasons are usually quoted as being responsible for the decrease in oxygen transfer with increasing *MLSS* concentration:

a) Increase in apparent viscosity (van der Roest et al. (2002), Krause (2005))

b) Elevated coalescence behavior (Germain et al. (2005))

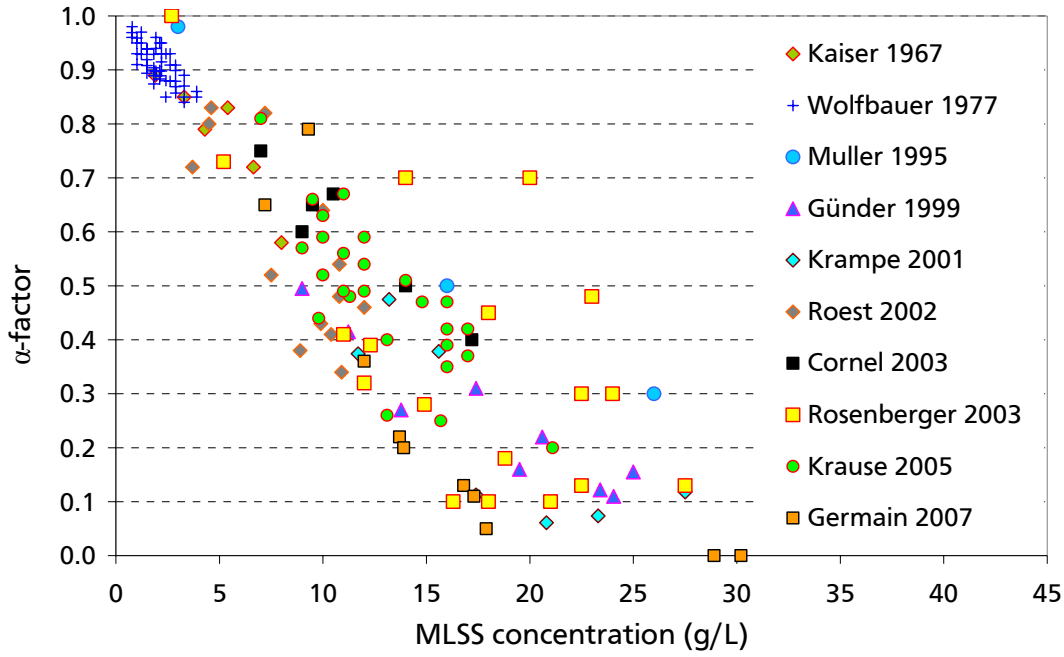


Figure 11: α-factor against MLSS concentration

Despite apparent viscosity of activated sludge often being quoted as responsible for the decrease in the α-factor, systematic studies are scarce and no standard method exists for determining the apparent viscosity in sludge. Therefore, the results of different studies are difficult to compare, since different viscosity measurement devices or different setup configurations (e.g. temperature) have been used. Figure 12 summarizes the results of apparent viscosity measurements for different *MLSS* concentrations at a similar shear rate (Krause (2005) and Krampe and Krauth (2003) at 40 s^{-1}; Rosenberger (2003) at 42 s^{-1}).

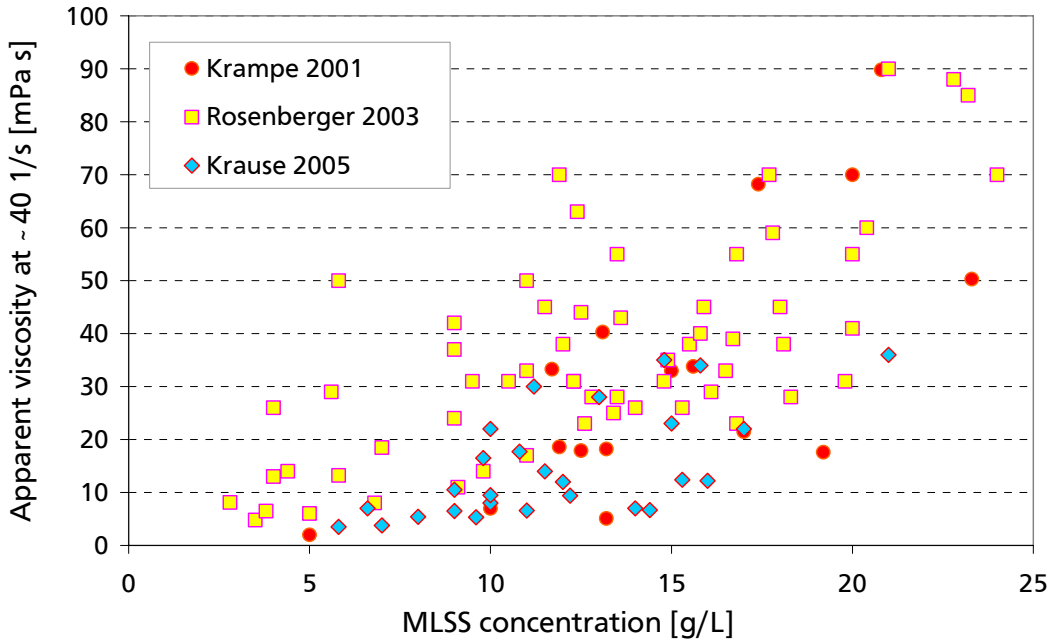


Figure 12: Apparent viscosity at different sludge concentrations

The results show great deviations, although the same measurement method was applied (rotational viscometer). Günder (1999) correlated the α-factor with the apparent viscosity (η) measured at a shear rate of 40 1/s, which was assumed to be the shear rate of rising bubbles, using the following equation:

$$\alpha = \eta_{40}^{-0,45} \qquad (3\text{-}17)$$

while Krause (2005) used the theoretically deduced equation

$$\alpha = \eta^{-0,32} \qquad (3\text{-}18)$$

Both equations result in an even wider α-factor spreading than observed with the *MLSS* concentration when applied to the apparent viscosity. While Germain et al. (2005) and Krause (2005) assumed that the apparent viscosity of the sludge does affect the diffusion coefficient, Günder (1999) neglects such a dependency. Assuming that the diffusion coefficient is affected, the theoretically deduced α-factor for fine bubble aeration systems turns out to be higher than for coarse bubble aeration systems (see Appendix, Section 11.5, page 123).

As mentioned in Section 3.1, activated sludge behaves like a non-Newtonian pseudoplastic fluid. Increasing shear stress leads to a decrease in viscosity. Consequently, an increase in turbulence, e.g. via an increase in airflow rate, should also result in a higher α-factor.

Concerning the promotion of coalescence by activated sludge Jin's results (Jin and Lant (2004), Jin et al. (2006)) indicated such a behavior. With increasing *MLSS* concentration, a decrease in gas holdup and liquid circulation velocity was observed. The decrease in gas holdup can be induced either by bubble coalescence or bigger bubble formation, caused by a lower liquid velocity (Section 3.2.2.1, Loubiere et al. (2004)) or additional downward forces induced by the flocs. Which effect led to a lower gas holdup in the end was not part of the investigation. However, the activated sludge floc characteristics (size, density) according to the experiments with particles (Deckwer and Schumpe (1983)) should promote bubble coalescence.

3.3.3.2 The role of sludge retention time in oxygen transfer

The sludge retention time, also called sludge age, mean cell residence time or solids residence time, is defined as the ratio of mass of sludge in the system to the mass of sludge produced per unit time (von Sperling and Chernicharo (2005)).

$$SRT = \frac{M_{SS}}{\frac{dM_{SS}}{dt}} \qquad (3\text{-}19)$$

with

M_{SS}	[kg]	Mass of sludge (suspended solids) in the system

In the steady state, the quantity of solids removed from the system is equal to the quantity of surplus sludge production (*SSP*). Neglecting the suspended solids concentration washed out through the clarifier in conventional activated sludge systems, the *SRT* can be written as:

$$SRT = \frac{V_R \cdot MLSS}{SSP} \qquad (3\text{-}20)$$

with

V_R	[m³]	Reactor volume
SRT	[d]	Sludge retention time

In this style it is used as the most important parameter for activated sludge design. It defines the degradation performance, the required reactor volume, the sludge production and oxygen demand. The *SRT* strongly depends on the Food to Mass (*F/M*) ratio applied to the system. However, in contrast to the *F/M* ratio that only depends on the mass of microorganisms and the *BOD* load, the *SRT* also changes with the suspended solids concentration in the influent and the temperature.

Generally it is observed that the α-factor in conventional activated sludge plants increases with increasing *SRT* (Figure 13).

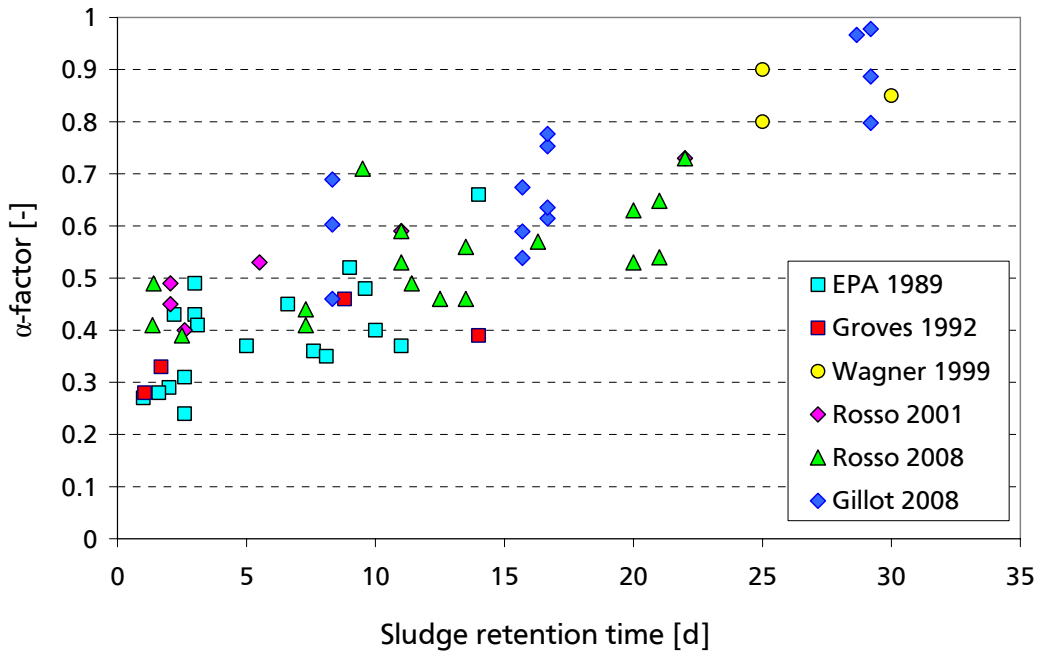


Figure 13: α-factor versus sludge retention time

It is presumed that with increasing *SRT* there is better degradation of dissolved substances, especially of surfactants, which negatively influence oxygen transfer (Rosso et al. (2008), Gillot and Heduit (2008)). Additionally, at high *SRT* (low *F/M* ratio) bacteria tend to degrade more complex organic material because of food lack (Tan et al. (2008)). However, large differences between α-factors are observed for similar *SRT* and usually the effect of the *MLSS* concentration is not considered.

A phenomenon related to the same effect of *SRT* can be observed in plug flow wastewater treatment plants. With increasing distance from the influent, the *F/M* value decreases and the α-factor rises because of preceding degradation during the process (EPA (1989)).

Long-term aeration batch experiments performed by Steinmetz on sludge from wastewater plants with different *SRT* also promote the positive effect of degradation and *SRT*. Sludge from a wastewater plant operated at high *F/M* ratio (~ 0.3 kg *BOD*/(kg *MLSS*·d)) showed a low α-factor in the beginning (0.66), which increased significantly with increasing aeration time (0.80). In contrast, the sludge from a wastewater plant with a low *F/M* ratio (< 0.06 kg *BOD*/(kg *MLSS*·d)) started at higher α-factors (0.8) and the change with increasing aeration time was small.

3.3.3.3 The role of diffusivity and respiration of activated sludge

As quoted in Section 3.3.1, the diffusivity of particles may influence oxygen transfer in a three phase system. That activated sludge flocs are diffusive to gases has long been recognized. The diffusivity of oxygen, as it is required for the aerobic degradation of organic material, was the work of several authors (Kossen (1979); Li and Bishop (2004)). Daigger et al. (2007) measured the oxygen profile in flocs with a size of 1 to 4 mm. The results showed a depletion of oxygen with increasing floc diameter in the floc. The penetration depth for dissolved oxygen depended on the external dissolved oxygen concentration and the activity

of the microorganisms present in the floc. However, it was not possible to determine the diffusivity of oxygen through the activated sludge floc. One of the major problems is the measurement of the undisturbed oxygen profile throughout the floc. How far the diffusivity of particles observed by Sun 1989 also affects the oxygen transfer coefficient in activated sludge suspension has not yet been studied.

The activity of activated sludge can be approximated using the respiration rate. In the calculation of the overall mass transfer, the respiration rate (Section 3.3.1) is introduced as a chemical reaction. As long as the respiration rate is constant and the oxygen concentration in the liquid phase is above 0 mg/L, it is assumed that the respiration rate has no influence on the determination of the oxygen transfer coefficient (Deckwer (1992)). Yagi and Yoshida (1975) investigated the effect of microbial respiration on the oxygen transfer coefficient and found no impact when comparing active and sterilized cell concentrations. The decrease in k_La often observed in a fermentation broth containing microbial cells is mainly due to the decrease in the specific interfacial area and not a decrease of k_L. Although Steinmetz (1996) observed that the respiration rate had an effect on the α-factor in some experiments, a general correlation between the respiration rate and the k_La value was not possible.

3.3.3.4 The interaction of surface active substances with activated sludge

The surfactants chosen for the clean water oxygen transfer tests in Section 3.2.4 were often selected according to surfactants present in detergents. From the results observed in clean water it was concluded that dissolved surfactants are also responsible for the decrease in the α-factor in activated sludge (Wagner and Pöpel (1996); Rosso et al. (2008)). Additional to the effect in clean water, Steinmetz (1996) studied the impact of washing agent addition ("Persil" and "Alio Compact") in the presence of peat and activated sludge from a paper mill. The results show that the negative effect of surfactants on oxygen transfer is reduced if particles are present which tend to adsorb the impurities. Unfortunately, the activated sludge used for the experiments was not adapted to the washing agent and therefore no conclusion on biological degradation could be made.

However, it should be mentioned that, since the 2004 European regulation on detergents (EU (2004), No 648), all washing active substances present in detergents discharged to the sewer system have to be aerobically biodegradable. If not, a special permission is required. According to the regulation, ultimate aerobic biodegradation means the level of biodegradation achieved when the surfactant is totally used by microorganisms in the presence of oxygen, resulting in its breakdown to carbon dioxide, water and the mineral salts of any other elements present (mineralization). White and Russell (1993), van Ginkel (1996) and Knepper and Eichhorn (2006) describe the pathways that surfactants are degraded by microorganisms. In this context, SDS, which is the most frequently found surfactant in wastewaters (Hebrard et al. (2009)), is an easily degradable substance that will be mineralized completely. From this point of view, the impact of surfactants present in detergents on oxygen transfer in a complete mixed reactor should be negligible.

3.3.3.5 The impact of EPS on oxygen transfer

As mentioned in the introduction EPS make up the largest fraction of the floc in activated sludge. Two different origins can be differentiated; one from the bacterial cell, due to metabolism, and one from compounds in the incoming wastewater. Many researchers found proteins, carbohydrates, nucleic acids and lipids as the main EPS components (Raszka et al. (2006)) which also corresponds to the main wastewater influent fraction (Nielsen et al. (1992), Raunkjær et al. (1994), Dignac et al. (2000), Sophonsiri and Morgenroth (2004)). Steinmetz (1996) observed a decrease in α-factor with increasing EPS concentration in the sludge and concluded that bacterial metabolism products may influence oxygen transfer. However, EPS mainly occurs inside the floc and consequently does not get directly into contact with the bubble. Hence the mechanism how EPS may influence oxygen transfer remains still unclear.

3.4 Further results on oxygen transfer relevant to the activated sludge process

So far, the effect of single substances, such as alcohols, electrolytes and organic surfactants, on the oxygen transfer has been mentioned. However, as quoted in Section 3.3.3.5, the wastewater influent is a highly heterogeneous mixture of organic and inorganic compounds. When the effect of raw wastewater on the α-factor is studied an overall depletion of around 55 % (α-factor ~ 0.45) is found (Kayser (1967), Steinmetz (1996)). The effect is usually explained by surfactants present in the influent. However, surfactants do not only derive from detergents. Amphiphilic lipids that e.g. are present in cooking oils are also surface active substances which enter the wastewater treatment plant via the lipid fraction. Chern et al. (2001) showed that soybean oil, whose major composition is amphiphilic lipids, lowers the oxygen transfer strongly. Since lipids make up 20 – 25 % of the organic material in the domestic wastewater (Quemeneur and Marty (1994)), it is conceivable that this fraction may have a strong influence on oxygen transfer as well.

In some cases it is argued that the α-factor changes during the day in a wastewater treatment plant (EPA (1989), Reichert (1997)). However, it is extremely difficult to determine the daily variation of α-factor in a wastewater treatment plant. Depending on the method applied the calculation of the k_La value in wastewater either requires steady state or constant respiration rate (see Materials and Methods). Choosing a steady state the hourly changing load will lead to different airflow rates in the system which, as shown before, influences oxygen transfer mechanisms. Even more complicate is to maintain a constant respiration rate at hourly varying sludge loads.

Finally the observations of Steinmetz (1996) regarding the effect of dissolved organic carbon concentration (DOC) have to be mentioned. Unexpectedly no relationship in α-factor with increasing DOC concentration in the sludge could be observed.

4 Materials and Methods

4.1 Oxygen transfer measurement methods

Two main ways of determining oxygen transfer in activated sludge in practice are:

a) the dynamic method (non-steady state method), which can be divided into the absorption method, also called the re-aeration or gassing-in method, and the desorption method (gassing-out method)

b) the offgas method

According to Gourich et al. (2006), the dynamic method is still the most commonly used. Its limitations and advantages have been described by various authors (e.g. Merchuk et al. (1990)). Using the dynamic method, the change in oxygen concentration is measured while saturation in the liquid is reached. The k_La value can directly be determined from the data using Equation 3-3. This presumes that the oxygen saturation concentration has been disequilibrated by either increasing or decreasing its concentration.

Using the absorption method, the oxygen saturation concentration can be depleted by adding sodium sulfite or by aeration with pure nitrogen gas during clean water measurements. The respiration of microorganisms is used to lower the oxygen concentration in activated sludge systems. However, depletion should stop at higher values than 0 mg/L oxygen in the liquid phase to avoid stress to the aerobic bacteria. Consequently, the concentration range for analysis is often quite limited (5 – 8 mg/L).

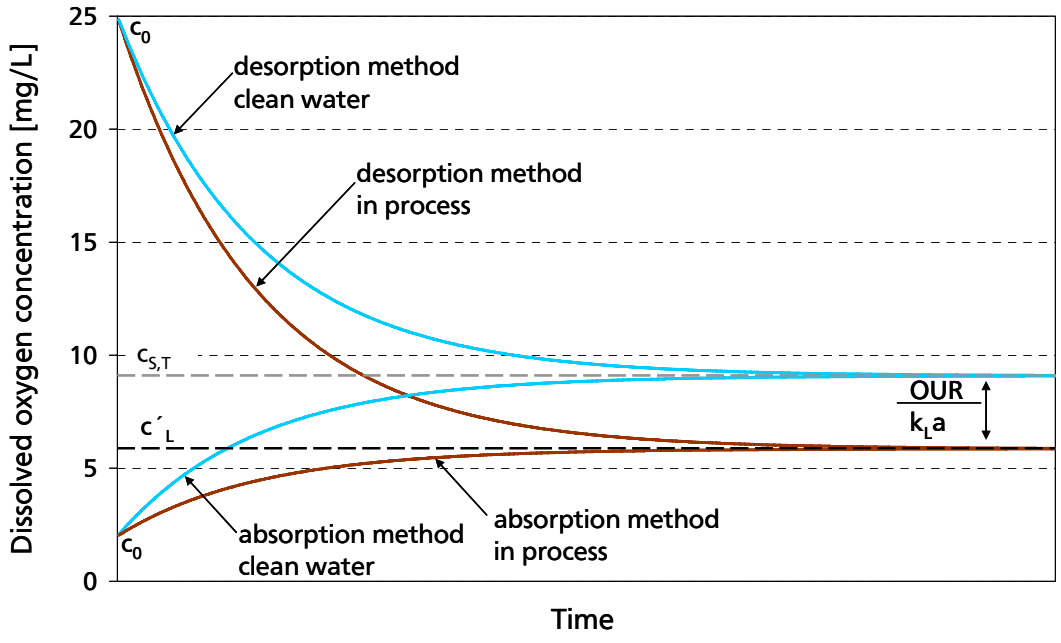


Figure 14: Plot of desorption and absorption method in clean water and under process conditions

During the desorption method, the oxygen concentration is raised by sparging pure oxygen into the system (Wagner et al. (1998)) or adding hydrogen peroxide (H_2O_2) directly to the sludge (Kayser (1979)). During normal aeration, the supersaturated oxygen desorbs from the

liquid phase (Figure 14) and the k_La is determined by the concentrations measured before saturation is reached. One advantage of this method is that the high concentration difference can be used for analyses (> 15 mg/L).

A critical issue when using the dynamic method is the oxygen probe response time (t_P). Usually, commercial oxygen electrochemical probes have a response time between 5 and 15 s. The dynamics of the oxygen sensor can only be neglected if the characteristic time of mass transfer ($t_f = 1/k_La$) is significantly higher (> 50 s). Another important factor is that maintaining a constant respiration rate during the dynamic method is imperative. This can be achieved by either shutting off the influent or by a constant inflow load.

The offgas method (see EPA (1989), Reichert (1997)) permits the continuous measurement of oxygen transfer rates in activated sludge systems without having any impact on the activated sludge. Using this method, in the steady state the oxygen transfer coefficient is estimated by dividing the gas phase mass balance by the aerated volume (Equation 4-1), thus measuring the concentration of oxygen (O_2) and carbon dioxide (CO_2) from the ambient air and the offgas.

$$k_L a_{20} = \left(1 - \frac{y_s \cdot (1 - y_e)}{y_e \cdot (1 - y_s)}\right) \cdot \frac{1.024^{(20-T)} \cdot Q \cdot \rho_O \cdot y_e \cdot 1000}{(c_{S,T} - c) \cdot V_L} \qquad (4\text{-}1)$$

with

y_s	[-]	Molar fraction of oxygen in the offgas,
y_e	[-]	Molar fraction of oxygen in the inlet gas
ρ_O	[kg/m³]	Oxygen density
c	[mg/L]	Oxygen bulk concentration
V_L	[m³]	Liquid volume

Capela et al. (2004) compared the absorption, desorption (H_2O_2) and offgas methods under different process conditions. The experiments revealed that the absorption method had the greatest deviation of the three methods. The offgas method yielded the best results and was the method of choice. However, it is limited to an oxygen saturation concentration in the media of < 50 % of the oxygen saturation concentration in clean water, since the difference between $c_{S,T}$ and the actual oxygen concentration (c) is used for to calculate the k_La. This leads to increasing uncertainties with decreasing differences if c is not determined exactly (Krause et al. (2003), DWA M 209 (2007)). Because of the high aeration rate of the crossflow used in membrane bioreactors, the oxygen concentration during the experiments ranged between 8 – 5 mg/L, while the oxygen saturation concentration was around 9.5 mg/L. Consequently, the offgas method was not appropriate, so the desorption method described by Wagner et al. (1998) was chosen as the appropriate method for determining the k_La.

4.2 The concept of membrane bioreactors

Figure 15 shows the three membrane bioreactor concepts used for the pilot-scale experiments. Reactors A and B were used for the greywater experiments and reactor type C was used for the wastewater experiments.

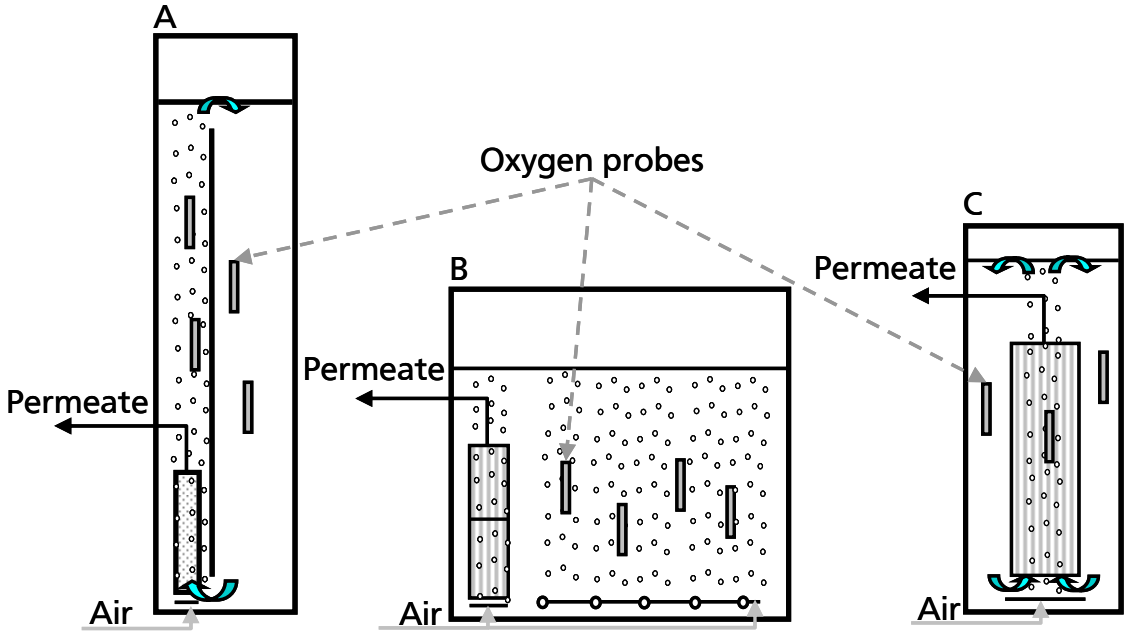


Figure 15: Membrane bioreactor configuration and oxygen transfer sensor position

4.2.1 Membrane bioreactor specifications for greywater experiments

Reactor A had a water volume of 2.6 m³ (2.5 m water depth) and was equipped with only one diffuser for membrane crossflow and aeration of the activated sludge. The aeration system induced a recirculation flow, which superseded the need for an additional mixing device (airlift reactor). Fine and coarse bubble diffusers were tested. The membrane area of the hollow fiber module was 20 m², with a pore size of 0.1 µm. Reactor B was equipped with five fine bubble diffusers, which were homogeneously distributed, and six coarse bubble diffusers for the crossflow. The water volume was 3.15 m³ (1.25 m water depth). The flat sheet membranes (12 modules) had an area of 24 m², with a pore size of 0.1 µm. The net flux in both systems was approximately 10 L/(m²·h). The greywater load was 1.7 $m^3_{greywater}/(m^3_{reactor}\cdot d)$ for reactor A and 2 $m^3_{greywater}/(m^3_{reactor}\cdot d)$ for reactor B. The organic load was 1.5 kg *COD*/d and 1.8 kg *COD*/d, respectively. The *SRT* ranged between 110 d (*MLSS* = 19.5 g/L) and 12 d (*MLSS* = 4.0 g/L).

4.2.2 Membrane bioreactor specifications for wastewater experiments

Reactor C had a water volume of 1 m³ (1.7 m water depth) and was equipped with only one diffuser for membrane crossflow and aeration of the activated sludge. As in reactor A, the aeration system induced a recirculation flow, superseding the need for an additional mixing device (airlift reactor). A fine bubble diffuser was installed below the membrane. The membrane area of the plate module was 10 m², with a pore size of 0.1 µm. The net flux was approximately 6 L/(m²·h). The wastewater load was 1.5 $m^3_{wastewater}/(m^3_{reactor}\cdot d)$. The organic

load was 0.9 kg *COD*/d. The calculated *SRT* ranged between 2 d (*MLSS* = 1.3 g/L) and 149 d (*MLSS* = 16.2 g/L). Two identical reactors were operated in parallel, differing only in their sludge concentration.

4.3 Experimental procedure

4.3.1 Pilot-scale experiments in greywater – Part I

The synthetic greywater composition was chosen according to the consumption of personal care products in private households in Germany (Chang (2007)). The mixture contained toothpaste, shower gel, soap, oil, shampoo, bubble bath, washing powder, other washing agents and softener. 3% raw wastewater was added to simulate hygienic contamination.

Table 3: Consumption of hygiene products in private households (per capita) and per day in Germany used as the recipe for synthetic greywater (Chang (2007))

Product	Quantity	Unit	% by weight
Toothpaste	2.53	mL/(C·d)	6.6
Shower gel	3.05	mL/(C·d)	8.0
Soap (fluid and solid)	0.34	g/(C·d)	1.0
Oil, lotion	0.26	mL/(C·d)	0.7
Shampoo	4.63	mL/(C·d)	12.1
Bubble bath	1.81	mL/(C·d)	4.7
Washing powder	15.15	g/(C·d)	39.7
Other washing agent	10.14	g/(C·d)	26.6
Softener	0.22	g/(C·d)	0.6

The total operation time of the pilot plants was 18 months and measurement of the oxygen transfer in the sludge took about 6 months. Clean water tests with drinking water were performed before beginning the inoculation with activated sludge and at the end of the total operation time. Four test series were performed:

a) Reactor A with coarse bubble crossflow

b) Reactor A with fine bubble crossflow

c) Reactor B with fine bubble aeration

d) Reactor B with fine bubble aeration and coarse bubble crossflow

Both membrane bioreactors were operated for the test series for about 3 months without sludge removal, until the maximum tested *MLSS* concentration was reached. After each test, the *MLSS* concentration was lowered by sludge withdrawal to the desired *MLSS* concentration for the next test. After withdrawal, the pilot plant was operated for 2–3 days under normal conditions before the oxygen transfer tests were started.

At the beginning of the experiments the water level was adjusted and the influent was switched off. Three to four oxygen sensors were placed in the reactor at different heights. Three different air flow rates were chosen (maximum, medium, low) at the same *MLSS* concentration for every test. Complete mixing of the sludge was guaranteed even at the

lowest airflow rate. Thus, no additional mixing devices were necessary for the oxygen sensors or for better mixing of the reactors. The experiments did not start until the oxygen concentration in the reactor stayed constant for at least 15 min and endogenous conditions were achieved. The time to reach endogenous respiration was approximately 90 - 120 min. Endogenous respiration was measured at the beginning and at the end of the experiments.

COD, anionic surfactants, pH and conductivity of the influent were measured before the influent was shut down. *COD*, anionic surfactants, pH, conductivity, *SVI* and capillary suction time (CST) parameters of the sludge were measured before the experiments started. Total solids (TS), volatile solids (VS), mixed liquid suspended solids (*MLSS*) and mixed liquid volatile suspended solids (*MLVSS*) were measured at the beginning and at the end of the experiments.

The airflow rate was measured with a thermal flow sensor TA10 (Hoentzsch GmbH, Waiblingen, Germany). The oxygen concentration was measured with 3 Evita Oxy 1100 sensors equipped with 0.4 and 0.2 mm membranes (Danfoss/Hach Lange GmbH, Düsseldorf, Germany) and an optical LANGE LDO sensor (Hach Lange GmbH, Düsseldorf, Germany). The signals were recorded every second and the OCA Parameter Estimation Program (AQUADATA, Braunschweig, Germany) was used to calculate the volumetric mass transfer coefficient (k_La) by nonlinear regression. The α-factor was calculated as the ratio of process water to clean water mass transfer coefficient, corrected to a temperature of 20 °C ($k_La_{20,MLSS}/k_La_{20,\text{clean water}}$).

4.3.2 Pilot-scale experiments in greywater – Part II

For these experiments, only reactor B was operated for four months without sludge withdrawal. Test series I started at an *MLSS* concentration of 24.7 g/L. As in part I, after each test the *MLSS* concentration was lowered by sludge withdrawal until the desired *MLSS* concentration for the next test was reached. Following sludge withdrawal, the pilot plant was operated for 2-3 days before the oxygen transfer tests were started. After 10 tests, when an *MLVSS* concentration of 4.2 g/L was reached, the reactor was operated for one month with continuous excess sludge removal to maintain the low *SRT* of approximately 12 d. Test series II started at an *MLSS* concentration of 4.0 g/L and was gradually increased up to 11 g/L without sludge removal. The measurement method and the analytics were identical to part I.

4.3.3 Pilot-scale experiments with real wastewater

Two experiments were performed with activated sludge and real wastewater influent:

a) Oxygen transfer measurements while the pilot plant was in operation

b) Oxygen transfer measurements after shutting down the influent for 24 hours

The wastewater was taken from the wastewater treatment plant in Eberstadt after it had passed through a 0.5 mm slit sieve. A constant influent load was reached throughout a settlement tank followed by a buffer tank (1 m³), which stored the wastewater for about 5 hours. By adjusting the permeate flow equal to the inflow, the level of the reactors was kept constant.

The experiments started one month after the pilot plant was seeded with activated sludge from the wastewater treatment plant in Eberstadt. The experiments were performed from low (2 d) to high *SRT* (149 d). This was achieved by keeping the influent load constant and operating the pilot plant without excess sludge removal. The measurement methods and the analytics were identical to the greywater experiments except for the use of different oxygen probes (iRAS automation GmbH, Bad Klosterlausnitz, Germany).

4.3.4 Greywater lab-scale experiments

Mass transfer coefficients were determined in a lab column to estimate the effect of the liquid and solid phases on the α-factor separately. The bubble column had a height of 1.25 m and a diameter of 0.30 m. The samples were taken from the membrane bioreactor A, which was operated at an *SRT* of 80 d, and from the membrane bioreactor B, which operated at an *SRT* of 12 d. A sample was also taken from the domestic wastewater treatment plant in Eberstadt. The plant operated at an *SRT* of 14 d, with an *MLSS* concentration of 4 g/L.

To study the effect of just solid matter, the sludge was "washed" several times with potable water until the supernatant was clear. This was necessary to reduce the impact of impurities in the liquid phase on the α-factor. The supernatant was taken from the membrane bioreactors while they were "in operation" to study the effect of the liquid phase alone. The supernatant was filtered through linen to avoid any influence from the flocs and reduce the impact of degradation provoked by microorganisms. The supernatant was separated from the "unwashed" sludge after an oxygen transfer test, and an additional oxygen transfer test was carried out on the supernatant only ("after test") to investigate the effect of stabilization on the liquid phase. The words in quotation marks describe the terms used in Table 6 and Table 9. The method applied was the same as described in the pilot-scale experiments.

Three oxygen probes (iRAS automation GmbH, Bad Klosterlausnitz, Germany) were used to measure the oxygen concentration. The airflow rate was measured with a rotameter (Kobold Messring GmbH, Hofheim, Germany) and a gas-meter (Ritter Apparatebau GmbH & Co. KG, Bochum, Germany).

4.3.5 Wastewater lab-scale experiments

As in the greywater experiments, the effects of the solid phase and the liquid phase were studied in a separate column. The bubble column had a height of 1.30 m and a diameter of 0.43 m and the same equipment was used as in the wastewater pilot-scale experiments. The total volume was kept constant at 100 L.

As well as the permeate and the supernatant directly taken from the pilot plant in operation, the wastewater sludge from the pilot plant was tested after 24 h aeration. One experiment included lowering the *MLSS* concentration to the desired lower concentration by withdrawing the sludge and replacing it with supernatant. Three gas flow rates were tested (1, 2, 3 m^3/h) in each experiment.

4.3.6 Iron Hydroxide Experiments

The bubble column used in this experiment was identical to the one used during the lab-scale wastewater experiments (1.30 m height and 0.43 m diameter). Three kilograms of ferric

chloride was mixed with 250 L of potable water in a separate vessel. A total of 100 g of bentonite powder was added to enhance the flocculation process. The pH was then adjusted to 8 with 1 molar sodium hydroxide, which increased the salt content to about 5500 mg/L. As the salt content also influences the oxygen transfer, the supernatant of the iron hydroxide flocs was replaced by potable water several times, until the salt content reached a concentration equivalent to that of potable water. The final salt content varied between 850 and 1100 mg/L. After sedimentation of the iron hydroxide flocs, 150 L of the supernatant was stored separately.

The experiments started at the highest iron hydroxide concentration. Three gas flow rates were tested, identical to those tested during the wastewater lab-scale experiments (1, 2, 3 m^3/h). A fixed amount of iron hydroxide flocs was removed from the system after each experiment and replaced with the stored supernatant. k_La and the α-factor were determined, as described previously. As well as the fine bubble aeration device used in the wastewater experiments, a coarse bubble aeration device was used.

A detailed list of the aeration devices including the range of airflow rates used in all of the studies can be found in the Appendix (Section 11.11, page 133).

4.3.7 Calculation of the Hydrostatic Floc Volume (HFV)

In a mixture of solid particles, the solid holdup can be easily determined by the bulk volume of the particles. However, if these particles tend to adsorb water, the bulk volume cannot be used. The sludge volume calculated by the dilution method represents the settling properties of sludge after 30 min and is used to estimate sedimentation behavior in the clarifier. However, it does not determine the volume occupied by the floc.

Therefore, a method was developed which seems to be able to determine the floc volume of iron hydroxide sludge. The following procedure was applied:

After each test, a 1 L sample was taken and stored in a settling column (7 cm diameter). The sedimentation process of the 1 L sample continued until the ferric hydroxide volume remained constant (36-48 h). The volume of the supernatant and the sludge was then measured. The volume of the water is termed the free water content and the volume of the flocs, the hydrostatic floc volume (HFV).

Table 4: Example for floc sedimentation

5/27/2009	12:30	0 h	start time	1000 mL/L
	14:45	2 h 15 min		380 mL/L
	15:45	3 h 15 min	~ 48 h	340 mL/L
5/28/2009	8:50	20 h 20 min		260 mL/L
5/29/2009	9:25	44 h 55 min		250 mL/L
6/2/2009	9:30	141 h		250 mL/L

The same procedure was then used for activated sludge. However, after 20 hours the sludge started to float because of denitrification. To prevent this, the sludge respiration was interrupted with cyanide, as described by Dobbs et al. (1995), using 0.1 g of cyanide per 1 g of biomass dry content. The free water volume and the hydrostatic floc volume could then be determined.

4.3.8 Calculation of the Sludge Retention Time

The *SRT* is defined as the ratio of mass of sludge in the system to the mass of sludge produced per unit time (Section 3.3.3.2). In practice, the *SRT* is used as a parameter to describe the operation in steady state. The rule of thumb is that this state is reached when the pilot plant is operated at least three times the *SRT* required. However in this dissertation in consequence of the experimental procedure the *SRT* was calculated differently.

Greywater experiments:
Since the sludge growth was recorded before the experiments started at the highest sludge concentration, the original definition of *SRT* could be applied by using the amount of sludge in the aeration tank ($MLSS \cdot V_R$) divided by the sludge production measured during the operation of the pilot plant.

To maintain a *SRT* of approximately 12 d before starting Test Series II in Greywater Experiments Part II, the reactor was operated for one month with continuous excess sludge removal (Figure 27, point 10), which conforms with the procedure in practice.

Wastewater experiments:
Since in the wastewater experiments the measurements started at the very beginning of pilot plant operation (after 1 month) and some devices, such as the settling tank, still had to be installed, it was impossible to reliably determine sludge growth. Therefore, the *SRT* was calculated using the empirical equation from the German Standard A 131 ATV-DVWK (2000), where the *SRT* is calculated as follows:

$$SRT = \frac{MLSS \cdot V_R}{L_{BOD} \cdot \left(0.75 + 0.6 \cdot \frac{c_{SS,in}}{c_{BOD,in}} - \frac{0.8 \cdot 0.17 \cdot 0.75 \cdot SRT \cdot 1.072^{T-15}}{1 + 0.17 \cdot SRT \cdot 1.072^{T-15}} \right)} \qquad (4\text{-}2)$$

with

SRT	[d]	Sludge retention time
$MLSS$	[kg/m³]	Mixed liquid suspended solids concentration
V_R	[m³]	Reactor volume
L_{BOD}	[kg/d]	*BOD* load
$c_{SS,in}$	[mg/L]	Suspended solids concentration in the influent
$c_{BOD,in}$	[mg/L]	*BOD* concentration in the influent
T	[°C]	Temperature

The change in *SRT* during the experiments was only caused by the growth of microorganisms and the suspended solids influent load. The influent flow was always kept constant and *BOD* variations reflect the fluctuation of raw wastewater from the municipal wastewater plant.

4.3.9 Analytical Methods

The sludge and supernatant samples were filtered through 0.45 µm membrane filters (Pall, Supor- 450). Chemical oxygen demand (*COD*) and anionic surfactants were determined with Hach Lange Cuvette Tests (LCK414, 514, 332). *MLSS*, *MLVSS*, sludge volume index (*SVI*), and endogenous respiration were estimated according to Standard Methods. CST tests were

performed with a capillary suction time filterability tester model 200 (Triton Electronics, Ltd., Essex, England). Conductivity and pH were measured with WTW LF 191 and pH 197 (Wissenschaftlich Technische Werkstätten, Weinheim, Germany).

Screening for fatty acid-like substances was performed with gas chromatography-mass spectrometry (GC-MS). The samples were first extracted with pentane, then with diisopropyl ether. To obtain a better response from the fatty acid like substances, derivatization with trimethylsulfonium hydroxide was used. An Agilent DB-XLB column and an HP 5973 Mass Spectrometer were used for detection (Agilent Technologies, Santa Clara, USA). The detection limit for the liquid samples was 0.01 - 0.1 mg/L, and for the solid samples, 0.5 - 5 mg/kg.

This method is not sensitive to carboxyl or sulphate head groups of the carbon chain. Consequently, no difference can be determined between fatty acids (carboxyl head group) and surfactants (sulfate, ether sulphate, etc. head groups). Thus, fatty acid-like substances here includes both groups of molecules.

4.3.10 Respiration Rate

The respiration rate was measured in hermetically sealed lab units (0.25 L) equipped with a magnetic stirrer (300 rpm) and an oxygen probe (WTW Wissenschaftlich-Technische Werkstätten GmbH, Weilheim, Germany) connected to a recorder. The sample was taken directly from the reactor before the oxygen transfer test started at saturated conditions. The lab unit was placed in a water bath that had the same temperature as the reactor. The respiration rate was calculated from the decrease in oxygen concentration over time and the measured *MLVSS* concentration of the sludge in the lab unit.

4.3.11 Calculating the α-factor

Three to four oxygen sensors recorded the change in oxygen concentration in the sludge at a constant airflow rate and *MLSS* concentration. From these records, the k_La was determined using nonlinear regression and an average k_La was calculated. The airflow rate was then changed and the procedure repeated at the same *MLSS* concentration. Three airflow rates were chosen for every test. Afterwards, the three average k_La values were plotted against the superficial gas velocity (*SGV*). If applicable, a linear trendline with its equation was calculated. This procedure was repeated for every *MLSS* concentration and the clean water test. Finally, the α-factor was calculated by dividing the trend line equation at a specific *MLSS* concentration by the equation obtained during the clean water test. As the x-variable, the three applied *SGV*s were inserted into the equation and as a result, three α-factors were achieved for each *MLSS* concentration. In the case of a non linear relationship between k_La and *SGV* the measured k_La was devided by the corresponding k_La calculated with the clean water trendline. The average of these three α-factors was plotted against the HFV, the *MLSS* and the *MLVSS* concentration. This was done since it was impossible to exactly repeat the same airflow rate for each test series. In contrast to the greywater experiments where the salt content was similar to that of clean water, the salt correction factor was applied in the wastewater experiments. This was necessary since the salt content was significantly higher than in clean water.

5 Results and Discussion

The following pages present and discuss the results obtained during experiments (Sections 5.1 - 5.3). In Section 5.4, new mechanisms are incorporated into a concept that describes the oxygen transfer phenomena observed in wastewater sludge. Finally, the consequences for use in practice are evaluated in Section 5.5.

5.1 Greywater experiments – Part I

Investigations started with oxygen transfer measurements in two membrane bioreactors that were fed with synthetic greywater. Because of its composition (see Materials and Methods), the greywater was suitable for studying the effect of high surfactant concentration in the influent on the α-factor in an activated sludge process.

5.1.1 Pilot scale results

Four test series were performed with different setup configurations (see Materials and Methods) to investigate the impact of diffuser type and reactor setup:

c) Reactor A with fine bubble crossflow (A, I)

d) Reactor A with coarse bubble crossflow (A, II)

e) Reactor B with fine and coarse bubble aeration (B, I)

f) Reactor B with only fine bubble aeration (B, II)

During the test series that lasted between three to five weeks each, the sludge parameters between reactor A and reactor B were almost identical (Table 5).

Table 5: Parameters analyzed before oxygen transfer experiments in the pilot plants (n = number of measurements, (±) standard deviation)

		Influent n = 23	Reactor A sludge; n = 24	Reactor B sludge; n = 22
COD	mg/L	310 (± 70)	10 (± 2)	10 (± 2)
Anionic surfactants	mg/L	70 (± 20)	0.3 (± 0.1)	0.3 (± 0.1)
Conductivity	µS/cm	940 (± 30)	860 (± 50)	880 (± 40)
pH	-	8.0 (± 0.3)	7.6 (± 0.1)	7.7 (± 0.1)
Loss on ignition	%	-	40 (± 7)	37(± 5)
SVI	mL/g	-	39 (± 6)	34 (± 6)
CST	s	-	6.9 (± 0.7)	7.0 (± 0.7)
Endogenous respiration	mg O_2/ (g *MLVSS*·h)	-	3 (± 1)	3 (± 2)

In contrast to wastewater sludge from other membrane bioreactors operating at high *SRT*, the greywater sludge was characterized by very low ignition loss (< 40 %), and very good settling and filtration (*SVI* < 40 mL/g, CST < 8 s). This was attributed to the high ratio of filterable solids to *COD* concentration (FS/*COD* ~ 0.33) in the influent, caused by abrasives in toothpastes (e.g. powdered white mica) or silicates in detergents used for softening water (e.g. zeolite). As expected, the anionic surfactant concentration in the influent was high and

the *COD* concentration was low compared to real wastewater. Approximately 95 % of the *COD* load and 99 % of the anionic surfactants load were removed by both bioreactors.

During clean water tests, the diffuser systems were analyzed for their volumetric oxygen transfer rates. A higher transfer rate was achieved with increasing airflow in all diffuser types (Figure 16).

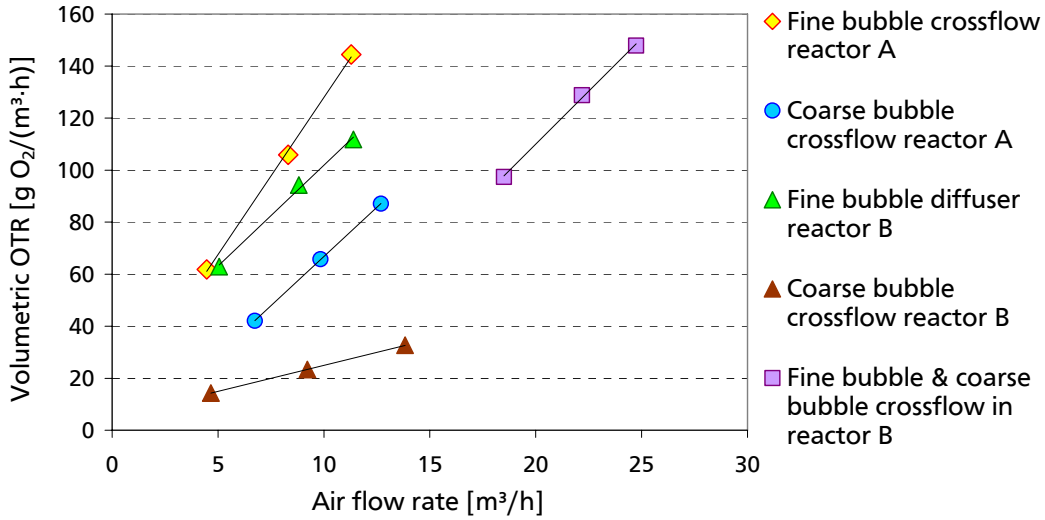


Figure 16: Volumetric oxygen transfer in clean water

Coarse bubble diffusers have lower volumetric oxygen transfer rates than fine bubble diffusers. In particular, the bigger bubble size produced by the coarse bubble diffuser led to a lower interfacial area and therefore to lower oxygen transfer. The influence of the water depth and the better hydraulic conditions of the airlift reactor are reflected by the generally higher oxygen transfer rates in reactor A than in reactor B when comparing the same aeration devices.

With respect to the volumetric mass transfer coefficients at different *MLSS* concentrations (Figure 17 - Figure 20), the k_La value at a specific airflow rate or superficial gas velocity (*SGV*) decreased steadily as the *MLSS* concentration raised. A linear relation of k_La was noticed, which indicates that the reactors operated either in the homogeneous or pure heterogeneous flow regime.

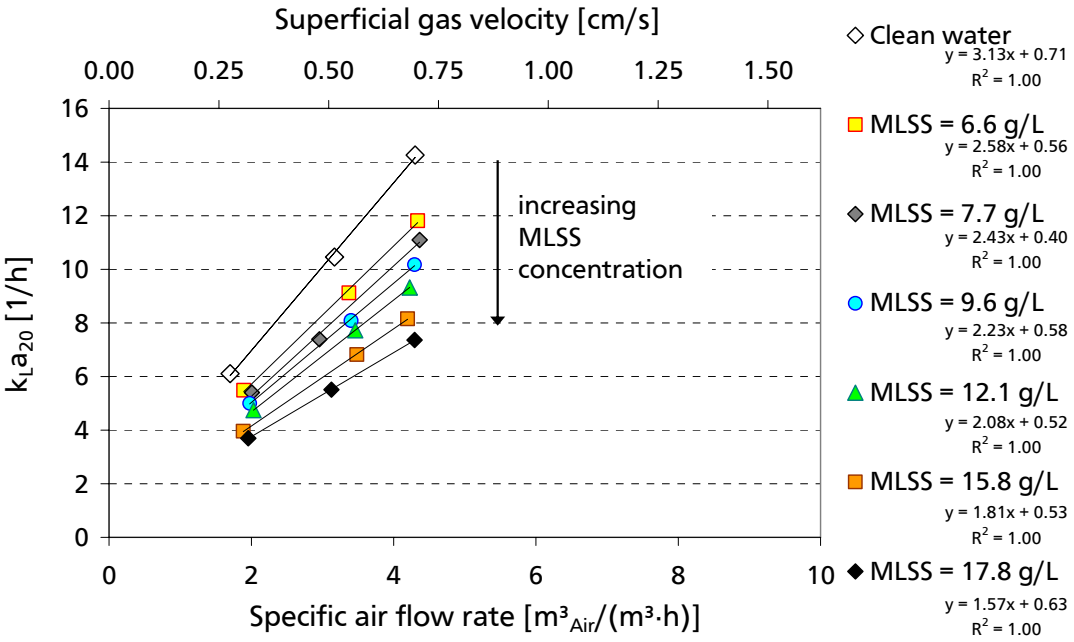


Figure 17: Volumetric mass transfer coefficient during fine bubble crossflow aeration (reactor A, I)

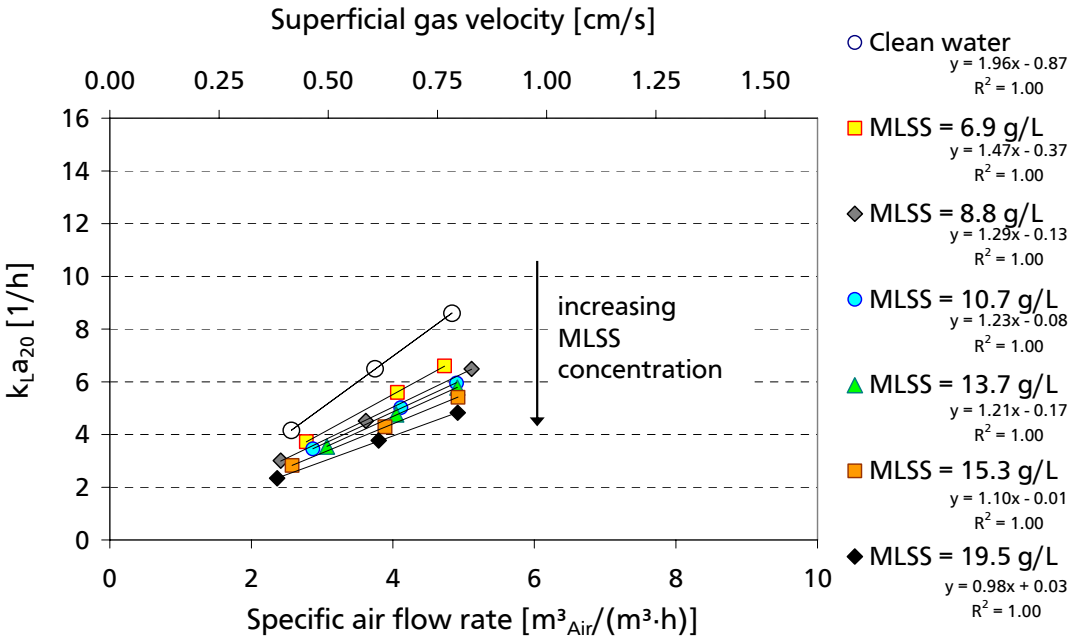


Figure 18: Volumetric mass transfer coefficient during coarse bubble crossflow aeration (reactor A, II)

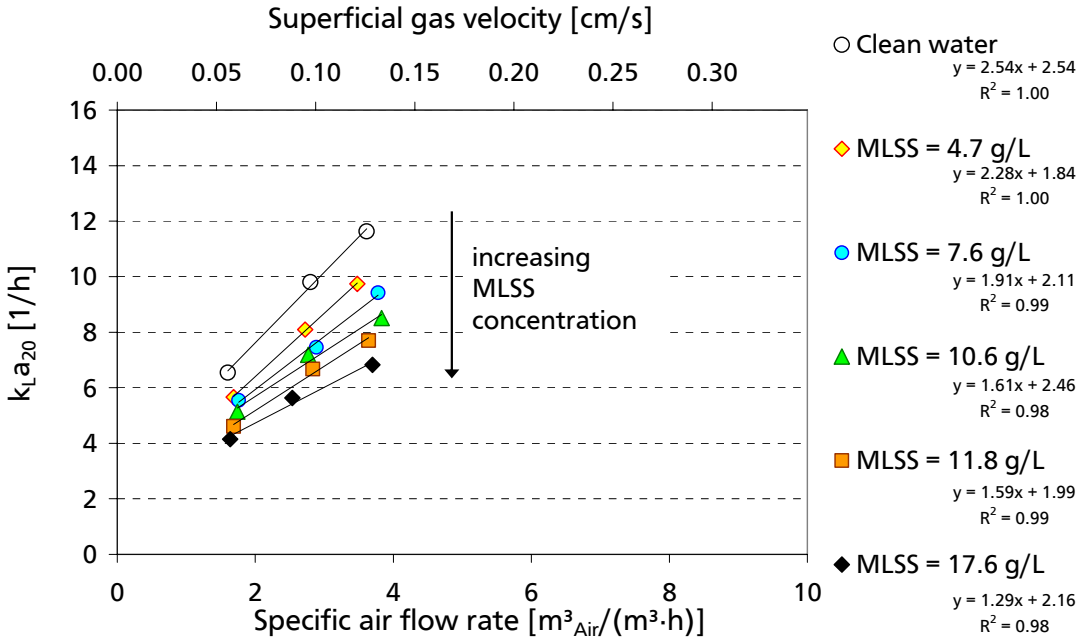


Figure 19: Volumetric mass transfer coefficient during fine bubble aeration only (reactor B, I)

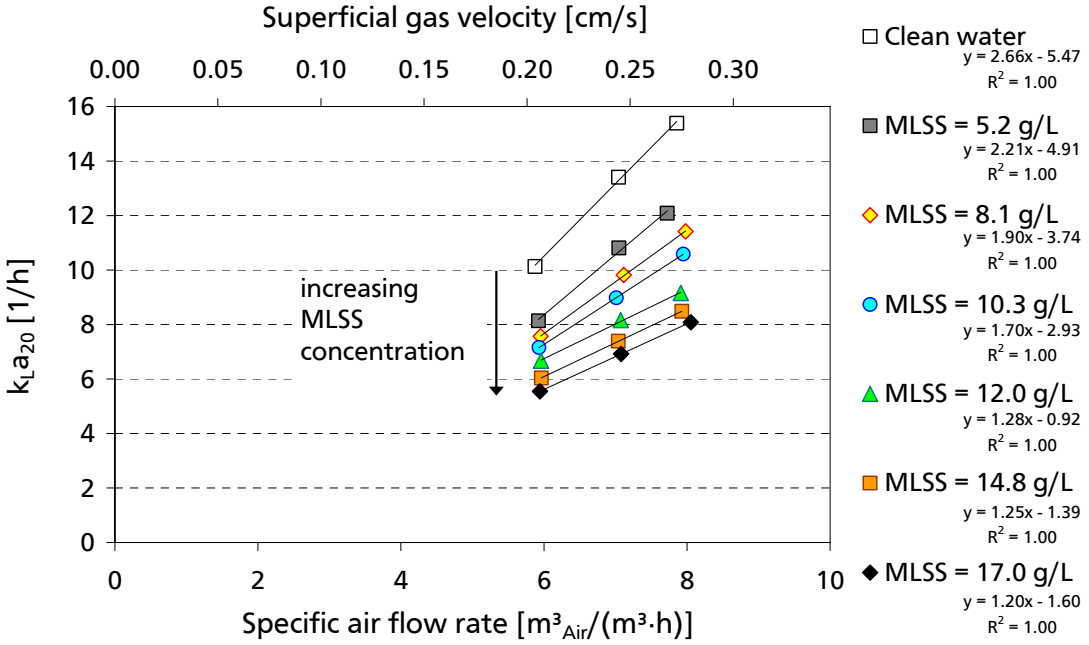


Figure 20: Volumetric mass transfer coefficient during fine bubble aeration and coarse bubble crossflow (reactor B, II)

In reactor B, with fine bubble and crossflow aeration (Figure 20) at an airflow rate of zero, according to the trendline equation all k_La had negative values. This can be attributed to the trendline equation summarizing two equations with different slopes, one for the crossflow aeration and one for the fine bubble aeration, as shown in Figure 16. As the crossflow aeration was kept constant at an *SGV* of approximately 0.15 cm/s during the experiments, an

extension of the trendlines is only permitted above an *SGV* of 0.15 cm/s. A comparison of all results reveals that every reactor configuration and aeration system had individual k_La characteristics.

After the k_La values were estimated, the α-factor was calculated by dividing the trendline equation for a solid concentration by the trendline equation obtained during clean water tests. The results are plotted in Figure 21. The standard deviation for all calculated α-factors versus the three air flow rates was 2.25%, with a maximum standard deviation of 6.5% for the fine bubble aeration at an *MLSS* concentration of 17.6 g/L in reactor B. It was interesting to find that the differences between the α-factor at a given solid concentration for all test series were small compared to former investigations (Figure 11) and that there was a fairly linear correlation between solid concentration and α-factor.

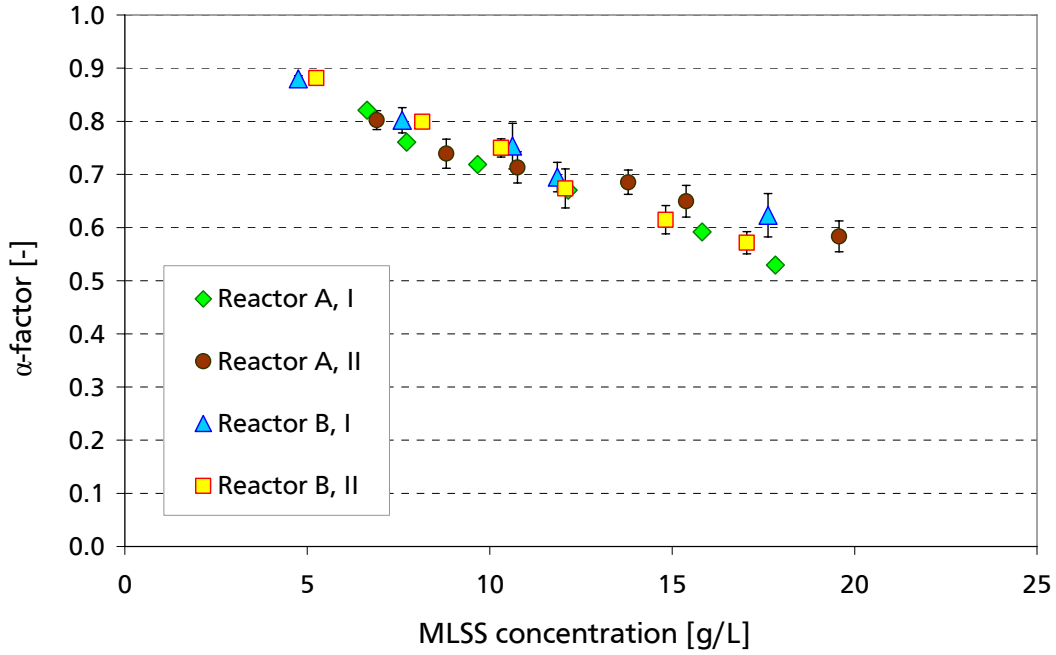


Figure 21: α-factor as function of the MLSS concentration (Greywater Experiments Part I)

5.1.2 Lab-scale results

The lab-scale experiments were performed to study the influence of the liquid and solid phases on the α-factor separately. The results of the greywater permeate and the greywater supernatant taken from the greywater pilot plant (*SRT* = 80 d) and the activated sludge, washed activated sludge and the supernatant of the activated sludge taken from the domestic wastewater treatment plant in Darmstadt-Eberstadt (*MLSS* = 4.0 (± 0.1) g/L, *MLVSS* = 2.8 (± 0.1) g/L, *SRT* = 14 d) are presented in Table 9 (standard deviation in brackets). The results show that the permeate had the same oxygen transfer coefficient as clean water. The greywater supernatant from reactor A, operating at an *SRT* of 80 d, had a lower impact on the oxygen transfer than the supernatant of the domestic wastewater plant (*SRT* = 14 d). The washed sludge (see Materials and Methods, Section 4.3.4) had a slightly higher α-factor than the unwashed sludge.

Table 6: α-factor of the lab-scale experiments, Greywater Experiments Part I

	Influent	Permeate	Supernatant in operation	Sludge unwashed	washed
Greywater (*SRT* 80 d)		1.01 (± 0.02)	0.91 (± 0.04)	-	-
Wastewater (*SRT* 14 d)	0.29 (± 0.02)	-	0.81 (± 0.02)	0.72 (± 0.03)	0.75 (± 0.01)

5.1.3 Discussion

The oxygen transfer measurements with greywater revealed a linear relationship between the k_La value and the *SGV* within a narrow range of this parameter. Such a linear interdependence is not mandatory. As introduced in Section 3.2.3.2, with increasing *SGV* the flow regime may change from homogeneous to heterogeneous, which causes a flattening of the k_La value. Additionally, with increasing solid concentration, the point of transition shifts to lower *SGV*, as described in Section 3.3.2. The highest *SGV* value in this study (0.8 cm/s) was significantly below the transition point value cited in literature (~ 4 cm/s). Therefore it is assumed that reactor configurations A, I and B, II (only fine bubble aeration devices, $d_B \sim 2 – 4$ mm) operated in the homogeneous flow regime (see Section 3.2.3.2). Configuration A, II (coarse bubble crossflow, $d_B > 20$ mm) operated in the pure heterogeneous regime. Configuration B, I (fine and coarse bubble aeration) consequently represents a hybrid system, where the membrane area has flow behaviors reflecting the pure heterogeneous regime, and the fine bubble diffuser area, the homogeneous regime.

As described in Section 3, the diffuser types and reactor configurations used in this study should lead to different gas holdup, bubble rise velocity, bubble wake behavior, affinity to surfactants, flow regime and consequently, considerably different k_La values. The results confirmed these variations (Figure 17 - Figure 20). However, these system characteristics had little effect on α-factor variation in greywater sludge at the same *MLSS* concentration (Figure 21).

This was surprising since current literature states that coarse bubble aeration systems generally have higher α-factors than fine bubble aeration systems (Stenstrom and Gilbert (1981), Rosso et al. (2008)). It is argued that high flow regime interfaces, as in coarse bubble aeration, are less affected by organic surfactant contamination and consequently show higher α-factors than low flow regime interfaces, such as in fine bubble diffusers. Results from this study revealed that the anionic surfactants were almost completely degraded (99 %) and the concentration in the liquid phase was close to the detection limit (0.2 mg/L) although the influent concentration was high (70 mg/L). Consequently, the explanation that α-factor decrease is caused by dissolved surfactants is not valid in this context.

The linear decrease of the α-factor with increasing *MLSS* concentration was not expected, since an exponential decrease of the α-factor with increasing sludge concentration is quoted in current literature (Günder (1999), Krampe and Krauth (2003), Rosenberger (2003), Krause (2005), Germain et al. (2007)). The exponential decrease is explained by the viscosity effect, as introduced in Section 3.3.3.1. However, this kind of viscosity effect is questionable. According to the calculations in Section 11.5, page 123 this effect should not only have lead

to an exponential decrease but also to lower α-factors for coarse bubble aeration systems compared to fine bubble aeration ones, even if the viscosity impact on the diffusion coefficient is excluded, as assumed by Günder (1999). Additionally the strongest impact of viscosity is observed at low values. This could not be confirmed by the experiments in this chapter.

The unequal process conditions expressed by the considerably different k_La values (Figure 17 - Figure 20) had little effect on the variation of the α-factors in greywater sludge at the same *MLSS* concentration (Figure 21). Consequently, the large differences of the α-factor at a given *MLSS* concentration obtained in activated sludge in this study and by other authors in Figure 22 seemed to be due to the different sludge characteristics like respiration rate, salt content, surfactant or EPS concentration.

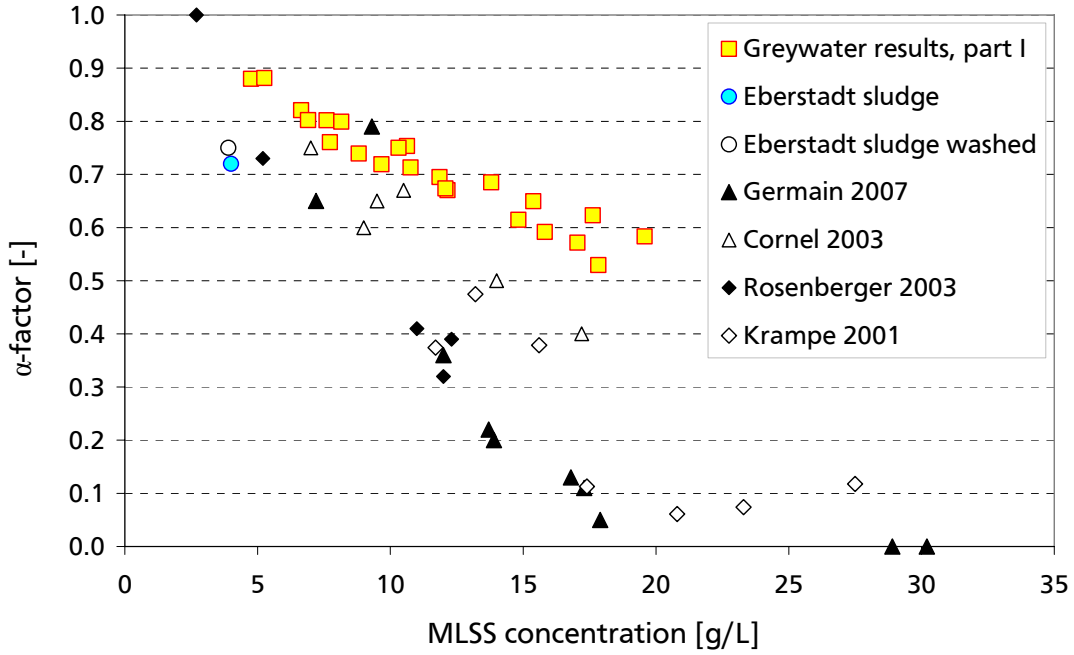


Figure 22: α-factor as a function of the MLSS concentration in this study and in literature

Krampe (2001) investigated the α-factor of membrane bioreactor sludge from a laundry, a malt house and a paper mill. Cornel et al. (2003) studied two full-scale wastewater membrane bioreactor plants, and Rosenberger (2003) measured 6 pilot scale and lab-scale reactors. Finally, Germain et al. (2007) tested ten biomass samples from both municipal and industrial, pilot and full-scale, submerged membrane bioreactors. It could be assumed that a comparison is not possible due to the different sludge origins and sludge characteristics or that the *MLSS* concentration is not the appropriate parameter for correlation of α-factors.

However, the low loss on ignition in this study was considerably different to other investigations. Correlating the same α-factors with the available *MLVSS* concentrations from other authors (Figure 23), there was a clear trend, irrespective of sludge origins. Thus, the question arose why this correlation fitted better and what the mechanism was behind this phenomenon that could not be explained so far.

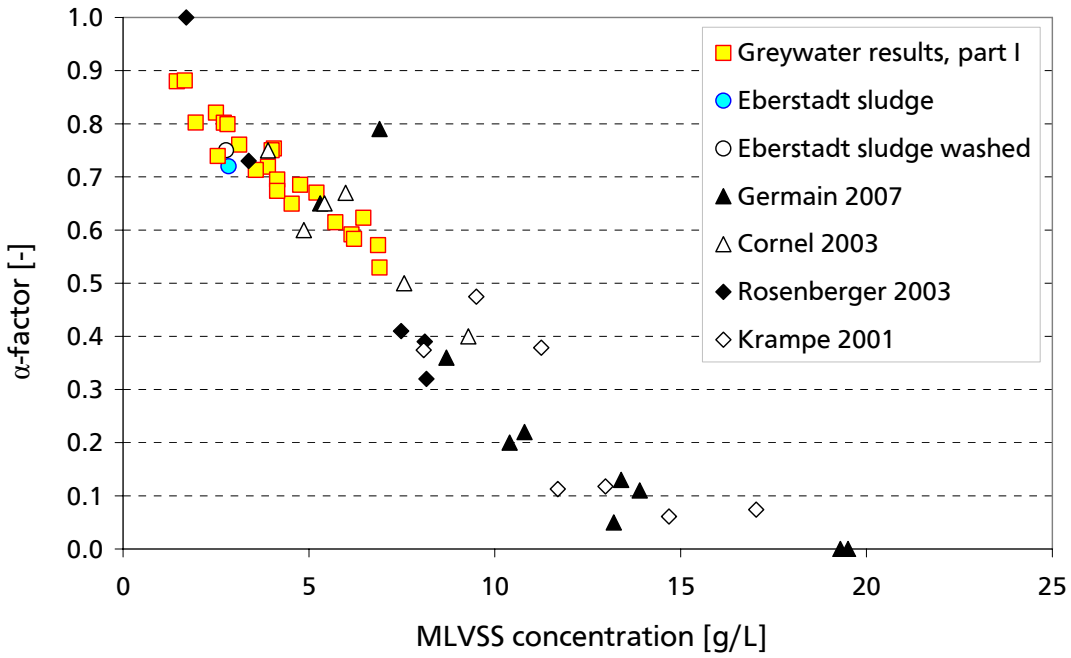


Figure 23: α-factor as a function of the MLVSS concentration in this study and in literature

5.1.3.1 Oxygen transport hypothesis at high SRT for different MLVSS concentration

Activated sludge is considered as a pseudo homogeneous medium with non-Newtonian pseudoplastic fluid properties in oxygen transfer studies (Yang et al. (2007)). Figure 24 is a photograph of an air bubble in greywater sludge with high and medium solid matter concentration.

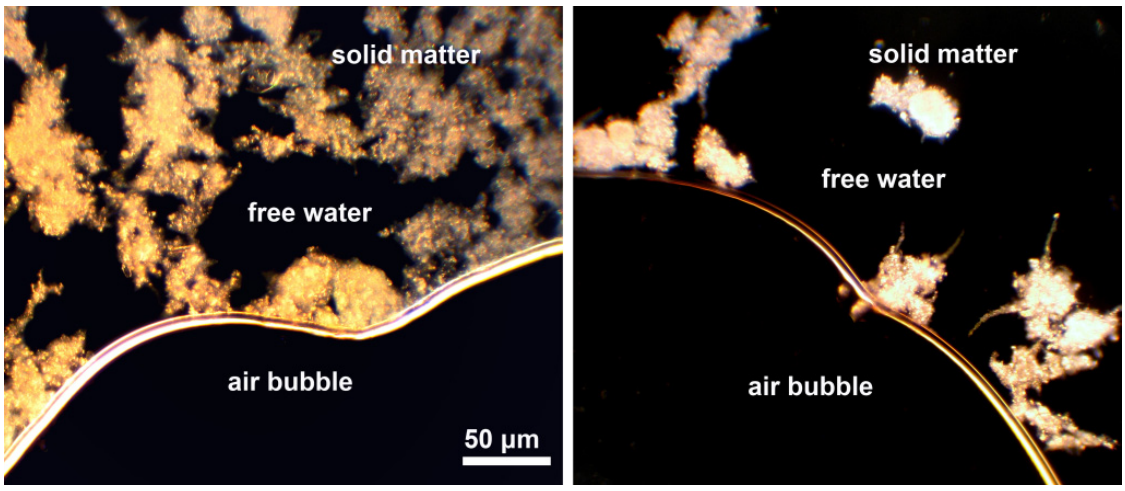


Figure 24: Free water content and bound water/solid matter content at the bubble interface at high (6.8 g/L) and medium (2.4 g/L) MLVSS concentrations

The floc forms a fraction that can be clearly separated from the free water content. It adapts to the bubble surface and reduces the free contact area between the bubble and the free water content. If the idea of a pseudo homogeneous medium is dismissed, interpretations of how the floc influences oxygen transfer into the free water fraction can be expanded to the observations regarding solids made in chemical engineering (Section 3.3.2).

The increase in solid concentration decreases the driving forces of liquid circulation, as observed by Jin and Lant (2004). This influences bubble formation (Section 3.2.2.1), coalescence behavior (Section 3.2.3.1) and the flow regime (Section 3.2.3.2). Additionally, gas holdup increases compared to the water content with increasing floc content, since at the same total volume the floc displaces water, thus shifting the flow regime towards the transition regime (Section 3.3.2). These explanations should lead to different α-factors for fine bubble and coarse bubble aeration systems, since coarse bubble aeration systems should not be affected by these mechanisms at all. Firstly, the flow regime is already heterogeneous and, second, liquid properties have only little to no effect on bubble formation and rising as introduced in Section 3.2.2 and 3.2.3.

Another mechanism other than the transfer mechanisms described above is possible, which is related to point 4 in Section 3.3.2 (physical chemistry of surfaces). Assuming the flocs tend to increase their concentration at the bubble surface or at least get in contact with the bubble surface because of the partially hydrophobic surface of flocs and the hydrophobic water/bubble interface (Figure 24), the interfacial area between the liquid and the bubble, a, could be reduced independently of the bubble size. The more water is bound by the flocs, the less free water is available for an undisturbed mass transfer from the gas to the liquid phase if the total volume is kept constant. Additionally, with increasing floc volume, oxygen transport from the gas directly to the diffusive floc could become more and more important.

In chemical engineering the volume fraction (solid holdup) is often used for oxygen transfer comparisons, since the solid concentration does not describe the solid holdup in a system properly (Deckwer and Schumpe (1983), Schumpe et al. (1984), Krishna et al. (1997), Freitas and Teixeira (2001)). As the *MLSS* and the *MLVSS* concentration only describe the sludge content in its dried form, it is hypothesized that the *MLVSS* concentration better correlates with the free water content and the floc volume (solid holdup) in activated sludge from different origins, which resulted in better correlation of the α-factors. The reason might be that the *MLVSS* fraction includes bacteria, protozoa and extracellular polymeric substances (EPS) which, to a large extent, consist of water (Raszka et al. (2006)). Therefore, the more water that is bound in a sludge sample by the organic matter, the larger is the occupied floc volume.

Using this hypothesis, the exponential decrease in the α-factor when correlated to the *MLSS* concentration might be explained as follows: with increasing *MLSS* concentrations at a constant *F/M* ratio, the *SRT* increases and the biomass growth decreases until it arrives at zero net growth, as reported by Laera et al. (2005). This leads to depletion of the volatile solids' content compared to the inert particle content. The lower organic content causes a lower floc volume, which is not correctly reflected by the *MLSS* concentration.

The inert particle content in a wastewater treatment plant is feedwater dependent and may vary greatly. Some plants, for example, do not use a primary sedimentation tank, which leads to a significantly higher suspended solids concentration in the influent. In our case, the greywater had large amounts of abrasive particles. This suggests that each sludge has an unique *MLSS* to *MLVSS* ratio, which leads to different floc volumes at the same *MLSS*

concentration. This may explain why a correlation of *MLSS* and the α-factor led to the wide spread of α-factors.

To give an example: The suspended solids concentration of wastewater sludge is usually 75 % organic and 25 % inorganic matter. The greywater sludge in this study was 40 % organic and 60 % inorganic matter. In Table 7, the floc volume is calculated using the assumption that the organic matter occupies a volume of 43 mL/g and the inorganic matter occupies only 3 mL/g for two *MLVSS* concentrations.

Table 7: Example calculation of the floc volume for greywater and wastewater sludge

	MLSS [g/L]	*MLVSS* [g/L]	MLISS [g/L]	Floc volume [mL/L]
Wastewater sludge I	6.7	5	1.7	220
Wastewater sludge II	13.4	10	3.4	440
Greywater sludge I	12.5	5	7.5	238
Greywater sludge II	25	10	15	475

It appears, that similar *MLSS* concentrations (13.4 and 12.5 g/L) can have quite different floc volumes (440 and 238 mL/L) while at similar *MLVSS* concentrations similar floc volumes are obtained. This could also explain the results of Steinmetz (1996) who observed a decrease in α-factor with increasing EPS concentration. As mentioned in Section 3.1, more than 50 % of the floc content can be attributed to EPS. Consequently the EPS concentration may not directly interact with the bubble but it significantly contributes to the floc volume and therefore negatively correlates with the α-factor.

It could be argued that the organic load (*COD*) is feedwater dependent as well: Kayser (1967) and Steinmetz (1996) proved its negative effect on the α-factor. Since 95% of the *COD* load in membrane bioreactors, which are commonly operated at $SRT > 25$ d, is usually degraded or adsorbed, its impact on the α-factor should be small. This was proved in the experiments with activated sludge and greywater sludge in separate columns. The permeate of the membrane bioreactor, which represents the dissolved phase of the supernatant, did not have any impact on the α-factor (1.01). Comparing the α-factors of the washed (0.75) and unwashed sludge (0.72) from a real wastewater plant operating at an *SRT* of 14 d, the results suggest only a small impact on the liquid phase but a major impact on the floc itself. Kayser (1967) tested the effluent of a wastewater treatment plant operating at low *F/M* ratio and achieved the same results. No impact of the wastewater effluent on the α-factor could be measured.

However, the α-factor of the wastewater supernatant (0.81; $SRT = 14$ d) was significantly lower than that of the greywater supernatant (0.91; $SRT = 80$ d). This can be attributed to better degradation of the impurities that influence the α-factor in the supernatant at high *SRT*.

5.1.4 Conclusions

a) High surfactant concentrations in the influent (70 mg/L) had little effect on the α-factor during non-steady-state aeration tests in a completely mixed sludge system with high *SRT*, since the anionic surfactant concentration in the reactor was low (0.3 mg/L).

b) Both reactors – although very different in their setup configurations – had a similar decrease of the α-factor with increasing *MLSS* concentration. Consequently, the design and aeration devices had no significant impact on the α-factors.

c) The substances which affect oxygen transfer in the supernatant were completely retained by the ultrafiltration membrane.

d) The conventional explanations for α-factor reduction in wastewater do not explain the identical behavior of fine bubble and coarse bubble aeration systems with increasing *MLSS* concentration.

e) A better correlation of the α-factors in this study and of other studies is achieved if the *MLVSS* instead of the *MLSS* concentration is used as a basis for comparison. It is hypothised that decisive parameters for the observations in this chapter are the floc volume and the free water content, which better correlate with the *MLVSS* concentration.

5.2 Greywater experiments – Part II

One aim of Greywater experiments - part II was to find a substance that is capable of adsorbing water and creating floc structures similar to those in wastewater sludge, and to investigate the impact of free water content and floc volume on oxygen transfer.

Another purpose was to investigate whether the ratio of *MLVSS* to *MLSS* concentration (ignition loss) would change at lower *SRT* (~ 12 d) and how this change would affect the α-factor.

Additionally to the surfactants quick test, a gas chromatography-mass spectrometry (GC-MS) screening on fatty acid-like substances was performed to characterize the surfactants that could lead to depletion of the α-factor in the greywater supernatant, in the permeate, or at the floc surface (see Material and Methods, Section 4.3.9, page 42).

Finally, oxygen transfer measurements in reactor B with only fine bubble aeration were repeated to check if the results were reproducible. Test series I started at an *MLSS* concentration of 24.7 g/L while test series II started after the pilot plant had been operating for one month at an *SRT* of 12 d at an *MLSS* concentration of 4.1 g/L.

5.2.1 Pilot-scale results

The analytical parameters of the two test series are presented in Table 8.

Table 8: Parameters analyzed during oxygen transfer measurements in greywater (part II) (n = number of measurements, (±) standard deviation)

		Influent n = 14	Test series I: No. 1 - 9 *SRT* 135 → 25 d n = 20	Test series II: No. 11 - 14 *SRT* 12 → 60 d n = 8
COD	mg/L	270 (± 50)	9 (± 2)	8 (± 1)
Anionic surfactants	mg/L	62 (± 13)	0.3 (± 0.2)	0.3 (± 0.2)
Conductivity	µS/cm	880 (± 70)	870 (± 20)	850 (± 40)
pH	-	7.9 (± 0.3)	7.7 (± 0.3)	7.9 (± 0.1)
Temperature		28 (± 1)	24 (± 1)	25 (± 1)
Loss on ignition	%	-	31 (± 4)	42 (± 4)
SVI	mL/g	-	28 (± 4)	45.0 (± 7)
CST	s	-	7 (± 2)	6 (± 1)
Endogenous respiration	mg O_2/ (g *MLVSS*·h)	-	3 (± 1)	4 (± 2)

The *COD* and anionic surfactant concentrations of test series II were the same as in test series I, whereas the loss on ignition and sludge volume index were higher in test series II. As is shown later, the loss on ignition increased with decreasing *SRT* in test series I, which is not reflected by the average values.

The α-factor results are plotted as a function of the *MLSS* and *MLVSS* concentrations in Figure 25 and 26 respectively and which include the results obtained previously.

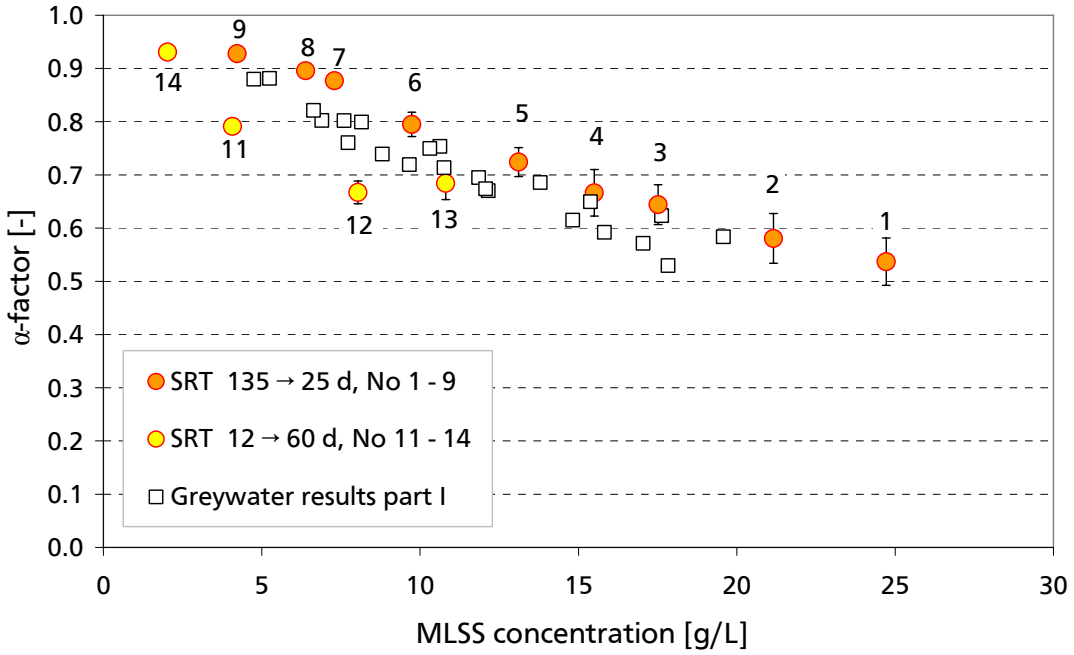


Figure 25: Development of the α-factor vs. MLSS from high SRT to low SRT and vice versa

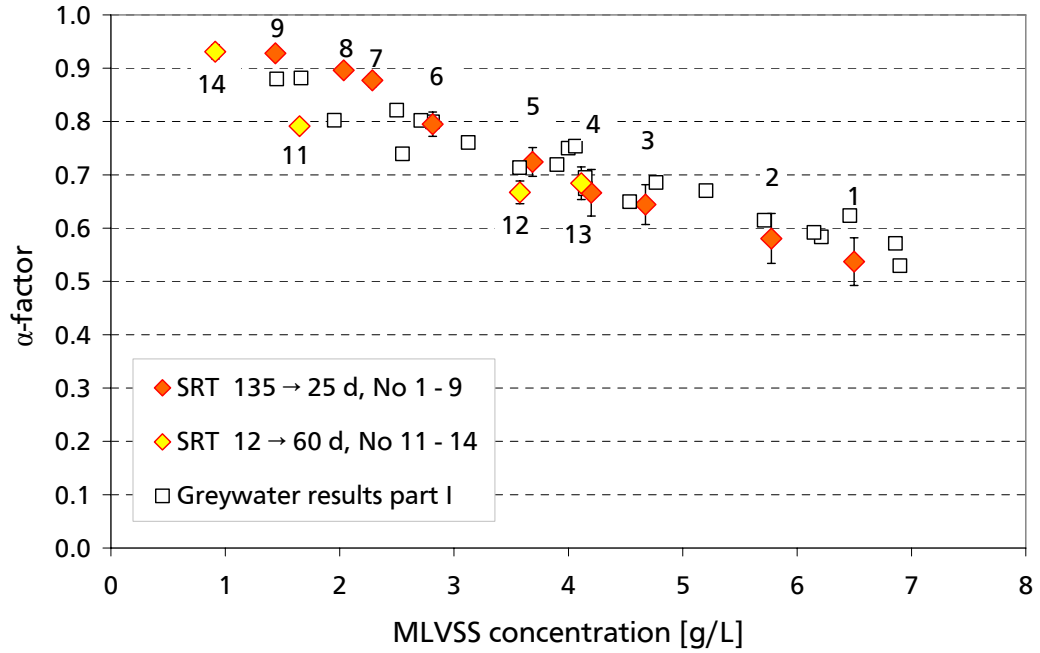


Figure 26: Development of the α-factor vs. MLVSS from high SRT to low SRT and vice versa

The standard deviation for all calculated α-factors versus the three air flow rates was 2.62 % with a maximum standard deviation of 7 % at an *MLSS* concentration of 24.7 g/L (No 1). The numbers correspond with the numbers in Figure 27 and represent the order of the experiments. Oxygen transfer was not examined at point 10. This point was included in Figure 27 to show the development of the loss of ignition during the one month operation at an *SRT* of 12 d. In test series I (*SRT* 135 → 25), a linear decrease in the α-factor with

increasing *MLSS* and *MLVSS* concentrations was observed. However, in test series II (*SRT* 12 → 60), the relationship was not linear when the α-factor was plotted as a function of the *MLSS* concentration. The biggest difference in the α-factor (0.2 points lower) in test series I (number 11) was at an *MLSS* concentration of 8.0 g/L. When the α-factor of number 11 was plotted against the *MLVSS* concentration the difference was only 0.08. Beyond this, the results suggest that a better correlation with the previous results is achieved if the *MLVSS* concentration is plotted against the α-factor.

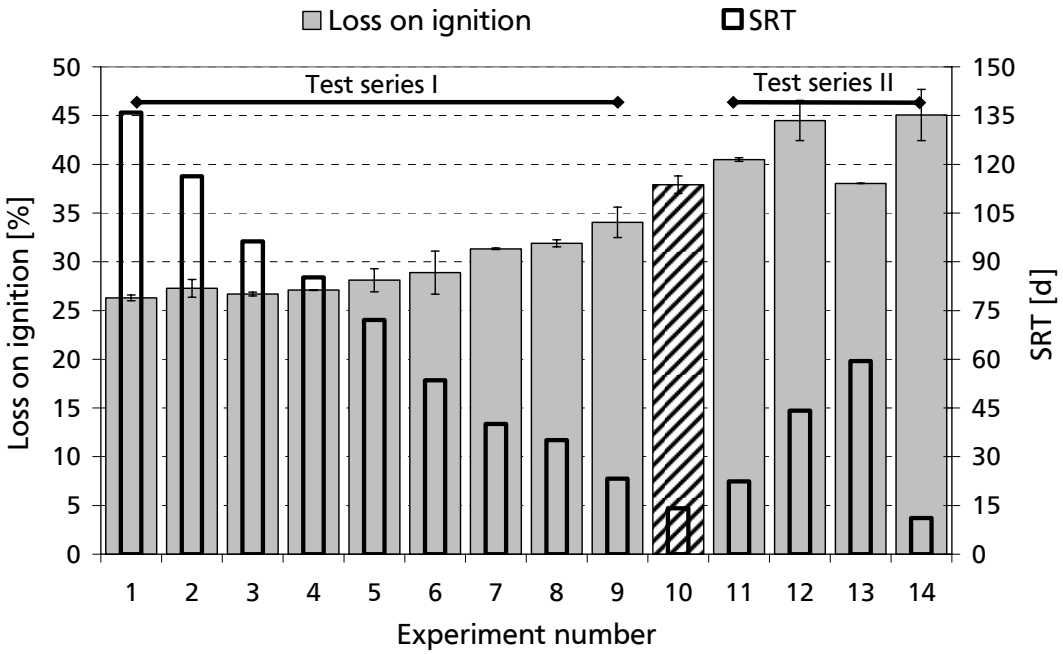


Figure 27: Loss on ignition vs. SRT

Figure 27 shows the development of the loss on ignition in relation to *SRT* during the test series I and II. Up to an *SRT* of approximately 50 d (number 6), the loss on ignition of the sludge remained fairly constant. When the *SRT* fell below 45 d, an increase in the loss on ignition was observed, which stopped again if the *SRT* was greater than 45 d (number 13). However, because the sludge was not in a steady state, different loss on ignition values were obtained for the same *SRT* (point 7, 32%; and point 12, 45%). Generally, the changes in the loss on ignition caused a change in the *MLSS*/*MLVSS* ratio.

5.2.2 Lab-scale results

As an extension of the lab-scale experiments presented in Greywater Experiments Part I, the experiments in this study concentrated on the greywater sludge at an *SRT* of 12 d. Table 9 summarizes the results from this study and the lab results from part I. The terms “in operation”, “after test”, “unwashed”, and “washed” are explained in the Materials and Methods, Section 4.3.4, page 40.

Table 9: α-factor of the lab-scale experiments, part I and II ((±) standard deviation)

	Influent	Permeate	Supernatant in operation	after test	Sludge unwashed	washed
Greywater (*SRT* 12 d)		1.00 (± 0.01)	0.79 (± 0.03)	0.93 (± 0.02)	0.82 (± 0.02)	0.87 (± 0.00)
Greywater (*SRT* 80 d)		1.01 (± 0.02)	0.91 (± 0.04)	-	-	-
Wastewater (*SRT* 14 d)	0.29 (± 0.02)	-	0.81 (± 0.02)	-	0.72 (± 0.03)	0.75 (± 0.01)

The greywater permeate had an α-factor of 1, irrespective of the *SRT* in the membrane bioreactor. In contrast, the supernatant of the membrane bioreactor, which operated at an *SRT* of 12 d, induced a lower α-factor than the supernatant taken from the membrane bioreactor at an *SRT* of 80 d. The impact was similar to that of the supernatant taken from the municipal wastewater plant, which operated at an *SRT* of 14 d. If the supernatant was withdrawn after measuring oxygen transfer in the sludge, the α-factor improved and reached values similar to those of the supernatant measured at an *SRT* of 80 d. In comparison to the unwashed sludge, the washed sludge had a slightly higher α-factor. Similar observations were made with wastewater sludge. The lowest α-factor was in the raw wastewater. No measurements in the greywater influent were possible because of intensive foaming.

5.2.3 Gas chromatography-mass spectrometry (GC-MS) screening results

Table 20 (see Appendix, Section 11.12, page 134) displays the results of the GC-MS screening results. The majority of the greywater influent was C12 fatty acid-like substances. This is in good agreement with the published data of Smulders (2002), who reported that the largest part of active washing substances are C12 anionic surfactants, such as sodium dodecyl sulphate (SDS). Besides that, a remarkable concentration of C16 and C18 fatty acid-like substances could be detected. These substances are typically present in oils, which are commonly used in body lotions.

The permeates and the supernatant at an *SRT* of 80 d did not contain any fatty acid-like substances. In the supernatant at an *SRT* of 12 d, only C16 and C18 fatty acid-like substances could be quantified. In the solid samples, the concentration of measurable components at the floc surface at an *SRT* of 12 d was always higher than at an *SRT* of 80 d.

5.2.4 Iron hydroxide experiments with fine bubble aeration

The hydrostatic floc volume (HFV) was determined after the iron hydroxide suspension had settled for 48 h (Materials and Methods, Section 4.3.7, page 41). Figure 28 demonstrates the relationship between the free water content or the floc volume and the suspended solids concentration. With increasing suspended solids concentration the floc volume increased and the free water content decreased linearly.

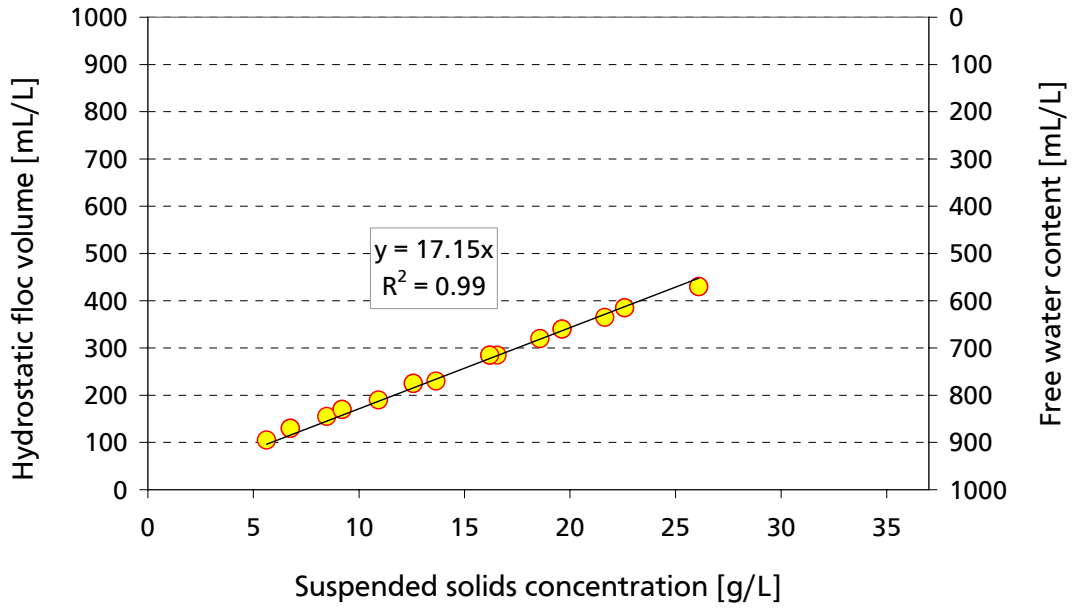


Figure 28: Relationship between suspended solid concentration, free water content and hydrostatic floc volume for iron hydroxide flocs

As per oxygen transfer measurements in greywater with increasing *SGV*, an increase in k_La values is observed for all suspended solid concentrations (see Appendix, Section11.16, page 142, Figure 68). At the same *SGV* the k_La value decreases with increasing suspended solid concentration and floc volume.

Figure 29 shows, that with decreasing free water content and the subsequent increase in floc volume, the α-factor decreases linearly.

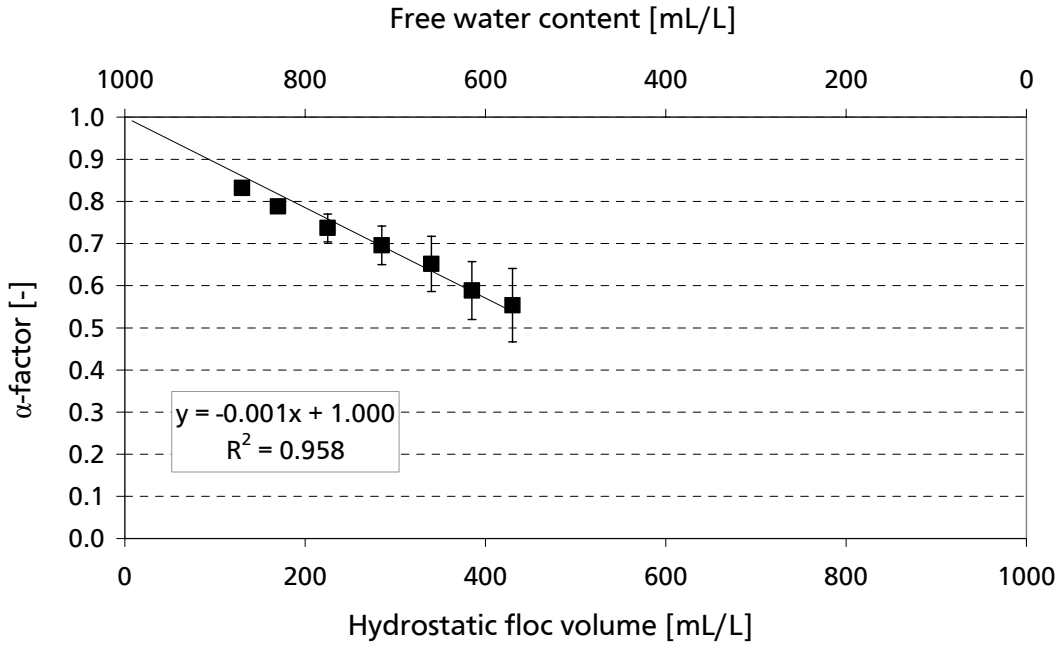


Figure 29: α-factor vs. free water content and floc volume with iron hydroxide

In the measured range the α-factor follows the equation α = HFV/1000. The average standard deviation for all experiments was ± 0.03. With increasing floc volume the standard deviation increased and reached the highest standard deviation at a floc volume of 430 mL/L (± 0.09).

5.2.5 Discussion

It has been hypothesized in Greywater Experiments Part I that the organic fraction of the floc (*MLVSS* concentration) regulates the free water content in sludge, and that with decreasing free water content or increasing floc volume, the α-factor decreases. That the free water content does influence the α-factor was shown by the iron hydroxide experiments. The results presented in Figure 29 indicate that an increase in floc volume decreases the oxygen transfer coefficient. Neither bacterial respiration nor surfactants or other organic matter present in the liquid phase or adsorbed at the floc surface are responsible for this phenomenon. A similar result was observed by van der Kroon (1968) with aluminum hydroxide flocs. The possible mechanisms range from increased bubble coalescence, decreased turbulence in the bubble wake and ascended collision forces caused by the presence of small particles, bigger bubble sizes produced at the orifice due to lower liquid circulation, to a decrease in interfacial gas/liquid area caused by a blockage of the floc at the bubble interface. However, a detailed analysis of which of these effects rules the suppression of oxygen transfer was not possible, since neither the gas holdup nor the bubble size distribution or bubble rise velocity could be measured. Evidence suggests that oxygen transfer suppression by hydroxide flocs and greywater sludge at high *SRT* are similar, since the α-factor in the greywater experiments also showed a linear relationship.

The experiments with the pilot plant revealed that with decreasing *SRT* an increase in the organic content occurred. Two reasons were mentioned in Section 5.1.3 and are related to the higher biomass growth rate at lower *SRT* and the inorganic particle load in the influent. However, a third mechanism is also conceivable and is related to the degradation and adsorption of organic compounds. With increasing *SRT*, slow-growing microorganisms that specialize in the degradation of slowly degradable substances can establish themselves, and the portfolio of more complex enzymes increases. Improved degradation of the organic substances adsorbed by the floc and present in the liquid phase occurs, which is reflected by a higher oxygen uptake rate at higher *SRT* (Tan et al. (2008)). Additionally with increasing *SRT* the floc surface available for adsorption increases, since the food to floc concentration decreases. Both effects result in a lower adsorptive floc load and higher adsorption rate and adsorption capacity, as observed by Phan and Rosenwinkel (2004). In contrast, with decreasing *SRT*, slowly degradable organic substances accumulate at the floc surface and are incorporated into the floc, leading to an increase in the loss on ignition.

It was not possible to quantify which of the effects (cell growth, degradation, adsorption) was the dominant one during the experiments. Section 3.1, introduced the concept that only a minor part of total organic floc content is present as active bacterial cell (5 – 20 %). The majority is represented by EPS. However, it is difficult to quantify which of these substances are just adsorbed slowly biodegradable substances that entered with the wastewater influent, as is the case of humic acids, or metabolism products of the cells themselves. Apart from the fact, that both mechanisms may take place at the same time.

However, the change in the loss on ignition from high to low *SRT* (Figure 27) resulted in different *MLVSS* concentrations and, consequently, different α-factors at the same *MLSS* concentration. It explains why the trend in Figure 25 was not linear when the *MLSS* concentration was plotted against the α-factor in test series II, and a better correlation was achieved when the *MLVSS* concentration was plotted against the α-factor.

Additionally it could be observed that the α-factors tended to be lower if the measurements were carried out from low to high *SRT*, even if they were plotted against the *MLVSS* concentration. It is conceivable that this trend is caused by an interaction between organic compounds adsorbed at the floc surface during low *SRT* (12 d) and the bubble interface. This is supported by the observation that dissolved substances had no effect on the α-factor, as they are not retained by the membrane filtration. Both lab-scale experiments with the permeate showed an α-factor of 1. Instead, it seems that long chain fatty acids adsorbed either to the floc or to small particles play an important role. They could be detected at higher concentrations during an *SRT* of 12 d in the sludge and the supernatant. This may also explain why the supernatant of the membrane bioreactor, which operated at an *SRT* of 12 d, induced a lower α-factor (0.79) than the supernatant taken from the membrane bioreactor at an *SRT* of 80 d (0.91).

The substances typically used to study the effect of surfactants on the α-factor (SDS, LAS, C12 fatty acids) were neither detectable in the supernatant, at the floc surface, nor in the permeate, even at a sludge retention time of 12 d.

5.2.6 Conclusions

a) With increasing floc volume and decreasing free water content, the α-factor is reduced in a linear way if iron hydroxide flocs were used. The same behavior could be observed in Greywater Experiments Part I and this chapter when the MLVSS concentration was correlated to the α-factor.

b) A better correlation between the α-factors in parts I and II could be achieved if the *MLVSS* concentration was related to the α-factors.

c) The change in *SRT* from higher *SRT* (80 d) to lower *SRT* (12 d) and back again led to an increase in the organic content of the floc at lower *SRT*. It could not be determined whether this change was caused by an increase in bacterial cell concentration or by organic compounds adsorbed to the floc or even by both effects.

d) Dissolved substances were not responsible for the lower α-factor measured in the supernatant at lower *SRT* (12 d).

e) This phenomenon and the slightly lower α-factors at lower *SRT* measured in the membrane bioreactors might be caused by the higher concentration of long chain fatty acid-like substances adsorbed by small particles and the floc surface, as detected using GC-MS.

f) Even at an *SRT* of 12 d, commonly used surfactants like SDS had no effect on the depletion of the oxygen transfer coefficient.

5.3 Wastewater experiments

One objective of this chapter was to compare the greywater results to real wastewater. In contrast to Greywater Experiments Part I and II, these experiments included oxygen transfer measurements while the pilot plant was in operation. Again, fatty acid-like substances were analyzed to study their impact on the α-factor. The lowest *SRT* studied was 2 d.

To investigate the effect of adsorption on the α-factor, oxygen transfer tests were performed with powdered activated carbon (PAC) added to clean water, 24 h aerated wastewater sludge from Eberstadt and wastewater influent.

Another task was to verify iron hydroxide results with activated sludge. To do this, the hydrostatic floc volume method had to be adapted (see Materials and Methods, Section 4.3.7, page 41). Additionally, the experiments with iron hydroxide flocs were extended to include coarse bubble aeration systems.

5.3.1 Floc volume results

Figure 30 pictures the floc volume in wastewater sludge determined with two different methods. The black triangles represent the results after 30 min sedimentation without dilution (conventional method). The grey rectangle pictures the floc volume after 48 hours of sedimentation (HFV method).

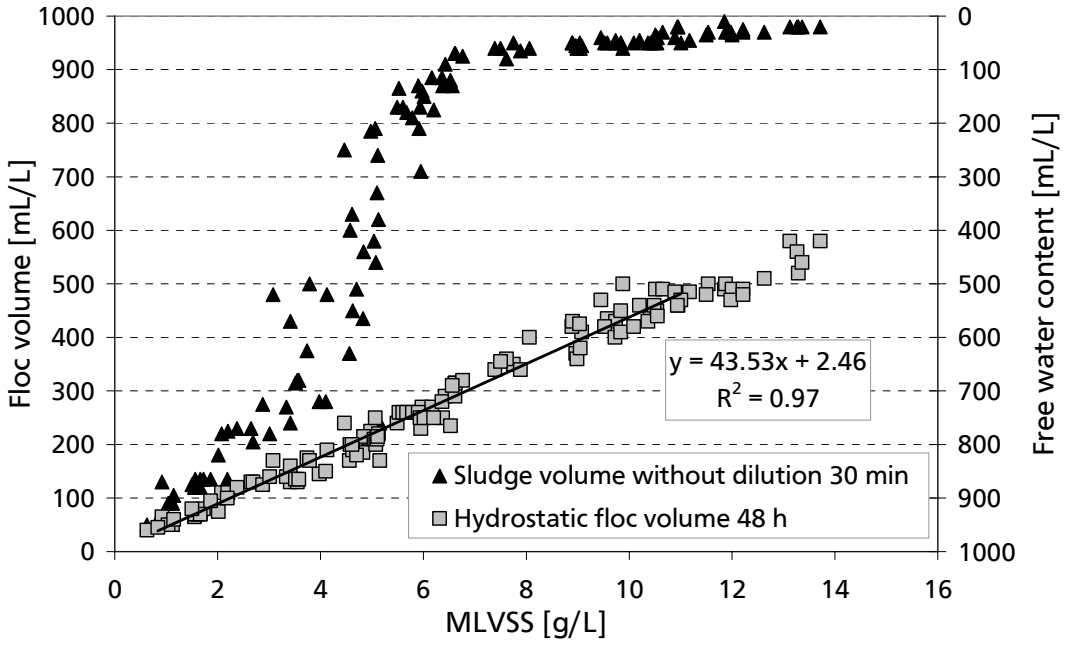


Figure 30: Development of the sludge volume after 30 min and 2 d correlated to the MLVSS concentration

The sludge volume increases with increasing *MLVSS* concentration in both cases. A linear correlation was observed for the HFV method up to a floc volume of about 500 mL/L at an *MLVSS* concentration of 11 g/L. At low concentrations, the 30 min method also showed a linear rising up to floc volume of 300 mL/L then increased exponentially until flattening occurred at higher concentrations (900 mL/L).

5.3.2 Pilot-scale results

The analytical parameters measured during the experiments are presented in Table 10. The anionic surfactants concentration in the influent (30 mg/L) was lower but the supernatant concentration (1.1 mg/L) was higher than in the greywater experiments (60 mg/L; 0.3 mg/L). Additionally, the *COD* concentration in the supernatant (56 mg/L) was significantly higher than in the effluent (26 mg/L), while the surfactant concentration was only slightly different. The pH in the reactor decreased from 7.7 to 6.7 compared to the influent, which was caused by the nitrification process and the relatively high ammonium concentration in the influent. The loss on ignition, temperature, and CST value stayed fairly constant. The specific respiration rate decreased during the experiments from 30 mg O_2/(g *MLVSS*·h) to 2.5 mg O_2/(g *MLVSS*·h), since with preceding experiments the *SRT* increased and the *F/M* ratio decreased gradually.

Table 10: Parameters analyzed during oxygen transfer measurements (n = number of measurements; (±) standard deviation)

		Influent n = 11	Supernatant n = 11	Effluent n = 11
COD	mg/L	500 (± 150)	56 (± 24)	26 (± 8)
Anionic surfactants	mg/L	30 (± 12)	1.1 (± 0.5)	0.8 (± 0.3)
Ammonium	mg/L	60 (± 16)	-	-
Conductivity	µS/cm	1400 (± 350)	1200 (± 200)	1300 (± 200)
pH	-	7.7 (± 0.1)	6.5 (± 0.5)	6.7 (± 0.4)
Temperature		20 (± 3)	20 (± 3)	20 (± 3)
Loss on ignition	%	-	82 (± 4)	-
CST	s	-	8 (± 2)	-

With respect to the volumetric oxygen transfer coefficient, the k_La value at a specific airflow rate or superficial gas velocity (*SGV)* did not always decrease as the *MLVSS* concentration increased (see Appendix, Section 11.15, page 140, Figure 65). A linear correlation of k_La to *SGV* was noticed up to an *MLVSS* concentration of 10 g/L. At higher *MLVSS* concentrations the relationship was not linear anymore (red trend line).

Figure 31 presents the α-factors in relation to the *MLVSS* concentration, the *F/M* ratio and the *SRT*. The numbers in the box represent the chronology of the experiments.

With increasing sludge concentration the α-factor is by trend reduced. The standard deviation for the calculated α-factors versus the three air flow rates was 3.7 %, with a maximum standard deviation of 12.3 % at an *MLVSS* concentration of 13.3 g/L. The *SRT* increased with increasing *MLVSS* concentration while the *F/M* ratio decreased. A non-constant relationship between the *SRT* and the *F/M* ratio was observed, which can be explained by the calculation of the two parameters. Besides the *BOD* load and the *MLSS* concentration, the *SRT* also depends on the suspended solids concentration in the influent and the temperature, while the *F/M* ratio only depends on the *BOD* load and the *MLVSS* concentration.

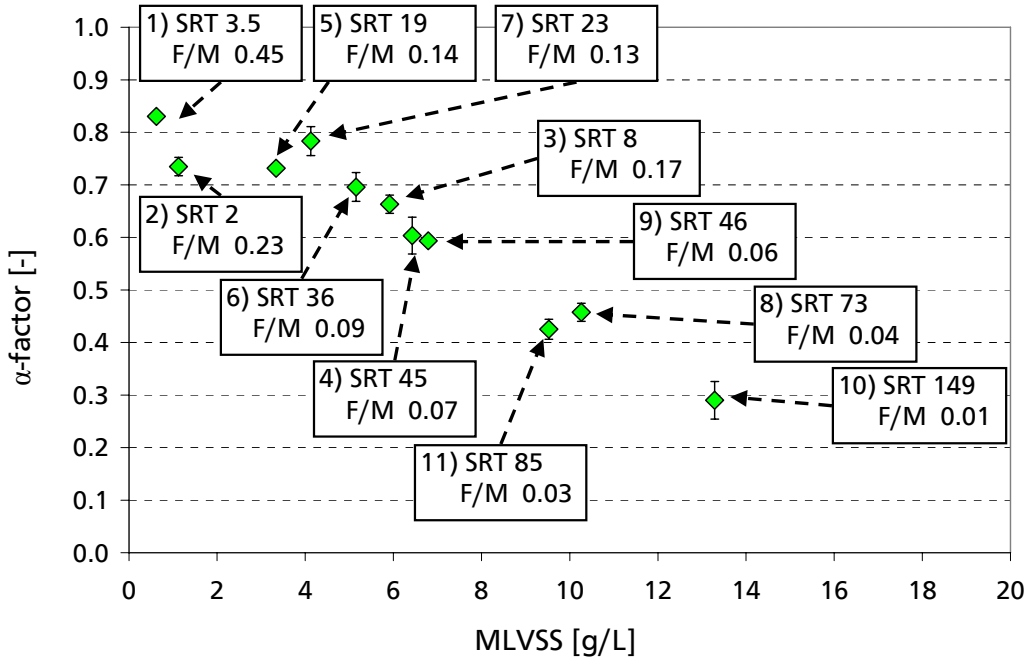


Figure 31: Development of the α-factor vs. MLVSS concentration during operation. Units for SRT = d; units for F/M = kg BOD/(kg MLVSS · d)

Figure 32 shows the same α-factors as in Figure 31 but correlated with the free water content and HFV, including α-factors measured after 24 h aeration while the influent was switched off. Except for 7 and 9, the values measured under these conditions were higher than the values measured during operation of the membrane bioreactors. Overall, the α-factor decreased with increasing HFV.

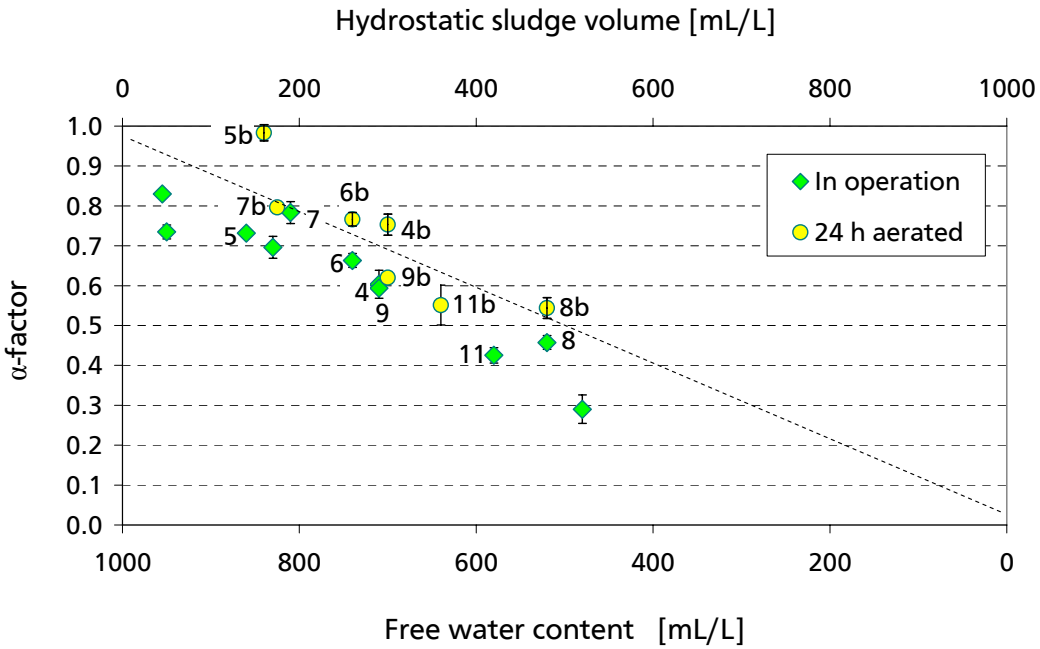


Figure 32: Development of the α-factor vs. HFV and free water content with 24 h aerated sludge and in operation

5.3.3 Lab-scale results

In the first lab-scale experiment, wastewater sludge was taken from the membrane bioreactor, which had been aerated for 24 h without wastewater influent. The experiment started at the highest *MLVSS* concentration of 14.1 g/L, followed by successive dilution with supernatant. The k_La results are displayed in Figure 66 (see Appendix, Section 11.15, page 140). With increasing *MLVSS* concentration and increasing HSV at a specific airflow rate, the k_La value decreased. At *MLVSS* concentrations higher than 10 g/L or HFV higher than 500 mL/L, the relationship between the k_La and the *SGV* was no longer linear.

The α-factors measured during these experiments are displayed in Figure 33. A linear decrease can be observed up to a HFV of 600 mL/L. The standard deviation for all calculated α-factors versus the three air flow rates was 11.3 %, with a maximum standard deviation of 19.9 % at an HFV of 590 mL/L.

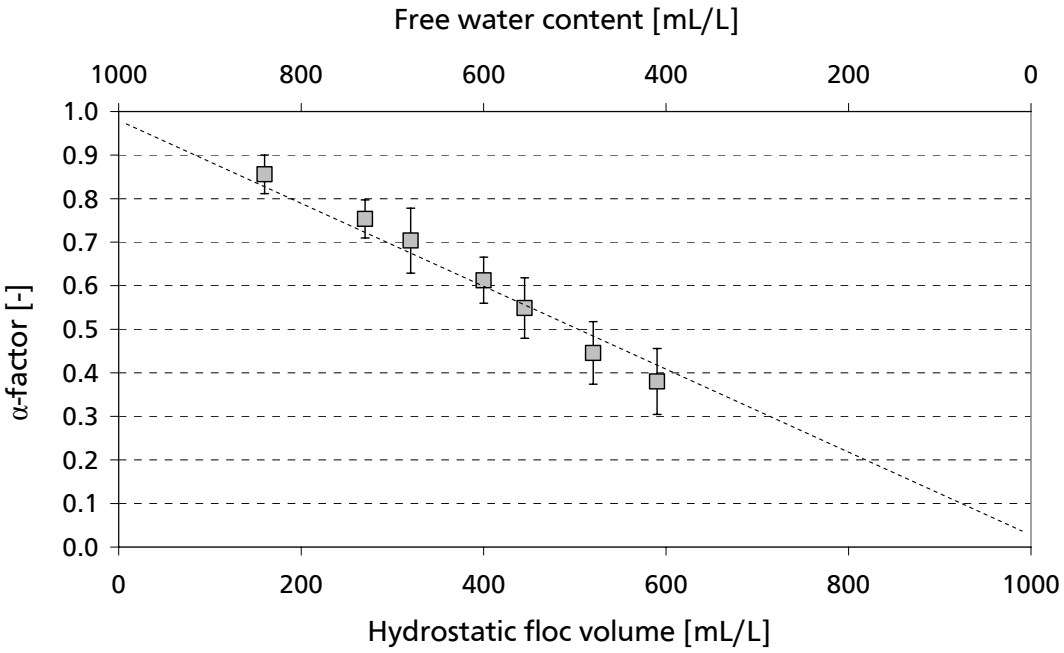


Figure 33: HFV and free water content vs. α-factors of diluted activated sludge

In the second lab-scale experiment (see Appendix, Section 11.15, page 141, Figure 67), the wastewater sludge was taken from the membrane bioreactor during its nine month operation after 24 h aeration without dilution. In these experiments, a non linear behavior between the *SGV* and the k_La was observed at *MLVSS* concentrations higher than 9 g/L (HFV = 430 mL/L).

The α-factors (Figure 34) by trend decrease with increasing HFV and decreasing free water content. The standard deviation for all calculated α-factors versus the three air flow rates was 10 %, with a maximum standard deviation of 26.7 % at an HFV of 540 mL/L.

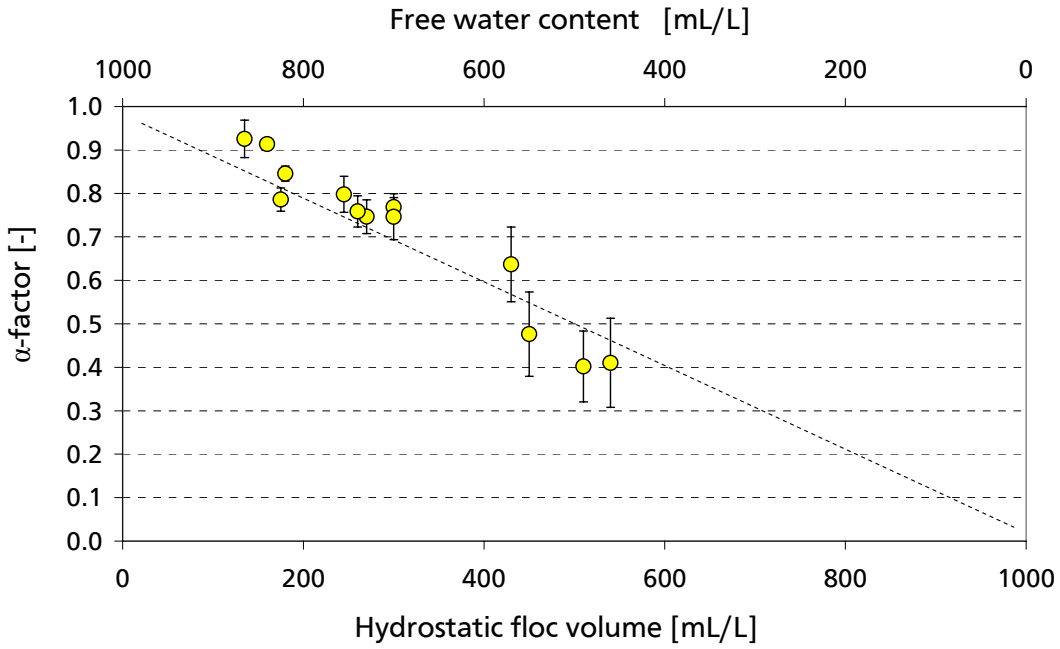


Figure 34: HFV and free water content vs. α-factor

A closer look on the results revealed that the deviation was not stochastic but systematic. At a higher flow rate, the α-factor was always lower than at lower flow rates.

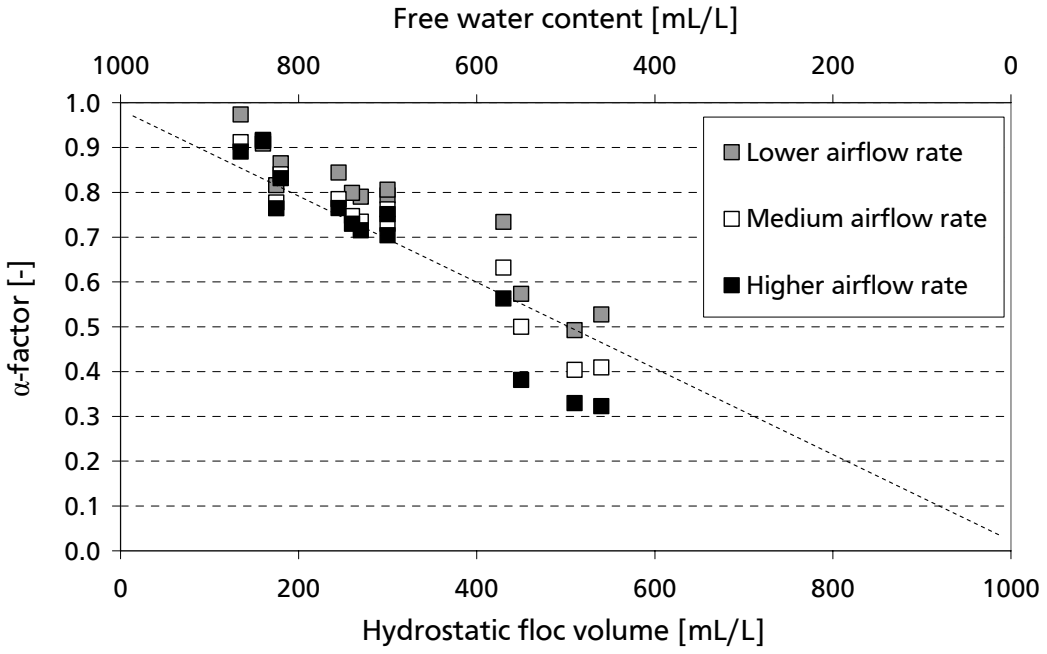


Figure 35: α-factor at different HFV and airflow rates

The effect seems to amplify with increasing HFV and *MLSS* concentration and was more pronounced for the experiments with high k_La values. It was observed at all oxygen transfer measurements, including the measurements with iron hydroxide flocs (see Appendix, Section 11.17, page 143 ff).

Additional to the sludge experiments, the permeate and the supernatant taken from the membrane bioreactor in operation on the same day that the pilot scale experiments were performed were tested. To complete the experiments, the wastewater influent to the MBR was periodically tested. The numbers in the table correspond to the membrane bioreactor experiments in Figure 31.

Table 11: α-factors in the lab-scale column ((±) standard deviation)

No.	*SRT* [d]	Permeate / in operation	Supernatant/ in operation	Influent
2	2	0.88 (± 0.04)	0.88 (± 0.02)	0.40 (± 0.04)
3	8	1.00 (± 0.01)	1.05 (± 0.03)	0.45 (± 0.05)
-	29	1.02 (± 0.01)	0.86 (± 0.01)	0.29 (± 0.02)
-	6	1.01 (± 0.01)	0.80 (± 0.01)	0.33 (± 0.02)
4	45	1.06 (± 0.02)	1.02 (± 0.01)	
5	19	0.96 (± 0.03)	0.92 (± 0.03)	
6	36	0.95 (± 0.01)	0.96 (± 0.01)	
7	23	0.97 (± 0.01)	0.99 (± 0.04)	

The results in Table 11 show that, except for an *SRT* of 2 d, the permeate had only little to no effect on the α-factor, with an average value of 0.98 (± 0.05). The results for the supernatant with an average value of 0.94 (± 0.09) were lower. The lowest α-factors were from the influent of the membrane bioreactor, showing an average value of 0.37 (± 0.07).

Finally, the effect of PAC addition to clean water, 24 h aerated sludge from Eberstadt and the wastewater influent on the α-factor was tested (Table 12). During the experiments with the influent, a screening on fatty acid-like substances was performed (see Section 5.3.4).

Table 12: α-factors of clean water, 24 h aerated sludge and influent with PAC addition including HFV values ((±) standard deviation)

PAC addition	-	+ 0.25 g/L	+ 1 g/L	+ 5 g/L
α in clean water		1.03 (± 0.01)	1.02 (± 0.01)	0.99 (± 0.02)
α in 24 h aerated sludge	0.93 (± 0.01)	0.89 (± 0.01)	0.88 (± 0.01)	0.76 (± 0.02)
α in raw wastewater	0.33 (± 0.02)		0.54 (± 0.06)	
HFV (PAC + clean water)	-	2 mL/L	6 mL/L	24 mL/L
HFV (PAC + sludge)	75 mL/L	80 mL/L	95 mL/L	150 mL/L

The addition of PAC to 24 h aerated activated sludge led to a decrease in the α-factor, while in clean water almost no effect could be observed. 1 g/L PAC in the influent noticeably increased the α-factor. In this case, the *COD* concentration decreased from 635 mg/L to 115 mg/L and the anionic surfactant concentration was reduced from 39.5 mg/L to 0.45 mg/L, which was even lower than detected in the permeate of the membrane bioreactor (Table 10). An addition of 5 g/L PAC to 24 h aerated sludge increased the HFV from 75 mL/L to 150 mL/L. The same amount of PAC in tap water occupied less than 25 mL/L.

5.3.4 Gas chromatography-mass spectrometry (GC-MS) screening results

To get a better understanding of how surfactants could have effected the suppression of oxygen transfer, further GC-MS screenings were performed. The results for the membrane bioreactor experiments are rearranged with increasing *SRT* (see Appendix, Section 11.13, page 135 ff.) and include the number of the corresponding membrane bioreactor test in Figure 31, the *SRT* and *F/M* ratio. The results for the experiments with PAC addition to the influent are pictured in Table 29 (see Appendix, Section 11.14, page 139)

In contrast to the greywater results, only very low concentrations of the commonly used C12 surfactants, like SDS or LAS, were detectable in the influent. The majority were C18 fatty acid-like substances, as they are the fatty acid fraction of lipids typically detected in wastewater (Quemeneur and Marty (1994), Dignac et al. (2000)).

In all membrane bioreactor permeates and the supernatants after 24 h aeration, no fatty acid-like substance could be detected and the supernatant samples taken in operation only sporadically showed C16/C18 substances in low concentrations. Regarding the sludge samples, the concentration at the floc surface after 24 hours aeration was always lower than during operation. No C12 fatty acid-like substances could be detected at the sludge surface at any *SRT*. In contrast, C18 fatty acid-like substances could be detected during all experiments. A significant reduction of these compounds at the floc surface could only be achieved if the sludge was aerated for 24 h and the influent switched off.

When the influent was filtered, hardly any fatty acid-like substance could be detected. The addition of PAC reduced the concentration of fatty acid-like substances that could be extracted from the unfiltered influent sample. No substance could be detected in the filtered sample after PAC addition.

5.3.5 Iron hydroxide experiments with coarse bubble aeration

In Greywater Experiments Part I, with increasing *MLVSS* concentration the α-factor decreased linear, independent of whether coarse or fine bubble aeration systems were used. At that time, the hydrostatic floc volume was not established yet and the idea that iron hydroxide flocs could have similar behavior to activated sludge flocs was still speculative. However, if the floc volume was responsible for the results in part I and iron hydroxide flocs cause the same effect as activated sludge, the experiments with coarse bubble aeration and iron hydroxide should have similar results to Greywater Experiments Part I. This is the focus of this chapter.

The k_La value at a specific airflow rate and superficial gas velocity (*SGV*) decreased steadily as the floc volume rose (see Appendix, Section 11.16, page 142, Figure 69). A linear relation of k_La was noticed, which indicates that the reactors operated in the purely heterogeneous flow regime. The bubble sizes produced by the coarse bubble aeration system in clean water included fine bubbles and coarse bubbles. The coarse bubble size was determined by visual observation and was around 40 mm.

The α-factor (Figure 36) decreased linearly with increasing floc volume. The standard deviation for all calculated α-factors versus the three airflow rates was 2.6 %, with a maximum standard deviation of 4.1 % at an HFV of 230 mL/L.

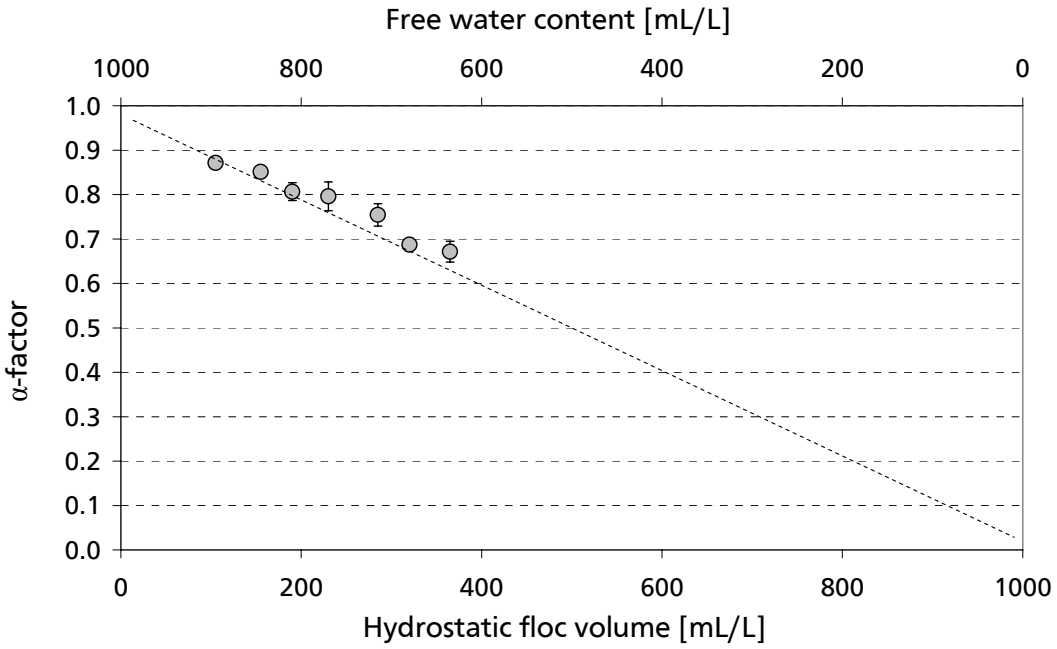


Figure 36: Development of α-factor vs. floc volume and free water content during iron hydroxide experiments with coarse bubble aeration

5.3.6 Discussion

One aim of the wastewater study was to compare the α-factors in wastewater sludge to those in greywater sludge. In Figure 37 and 38, the results are plotted against the *MLSS* and the *MLVSS* concentrations.

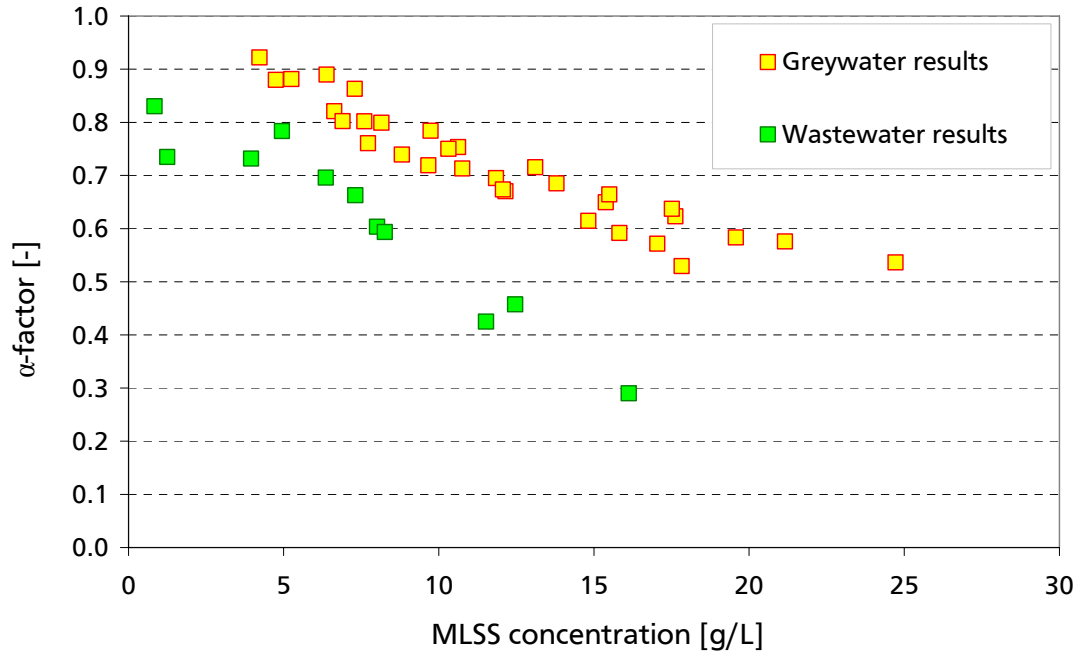


Figure 37: α-factor versus MLSS concentration in wastewater and greywater experiments

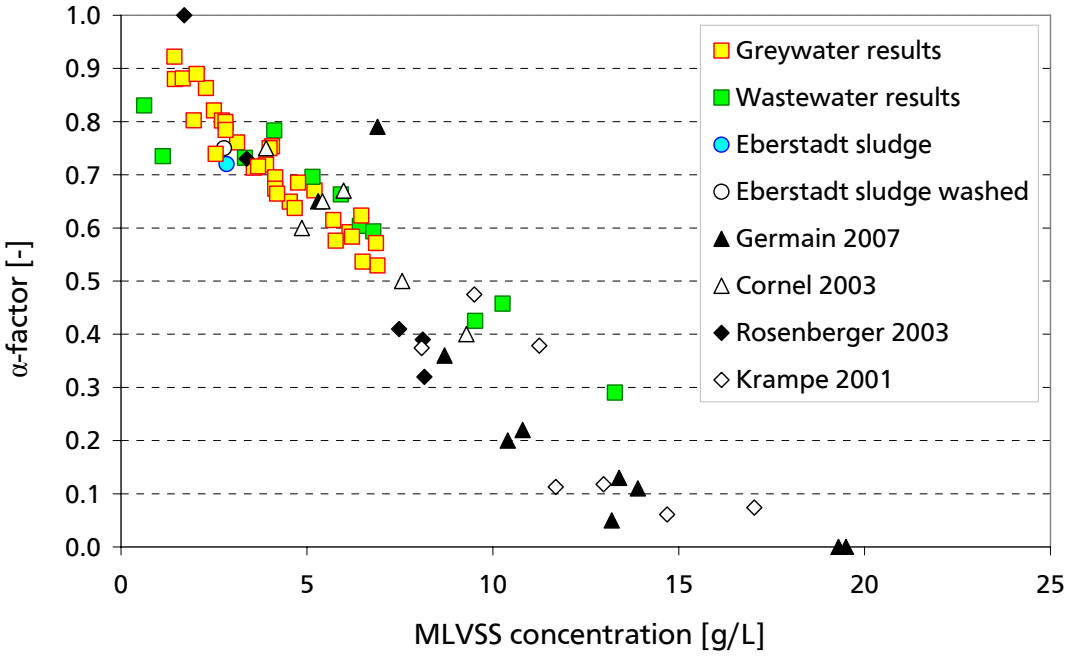


Figure 38: α-factor versus MLVSS concentration in wastewater and greywater experiments

Again, better correlation of the α-factors was achieved when the *MLVSS* concentration is used as a basis for comparison. Some explanations for this behavior were discussed in Sections 5.1.3 and 5.2.5. It was assumed that the *MLVSS* concentration better correlates with the free water content and the floc volume of sludge from different origins and that with increasing floc volume oxygen transfer is reduced.

Figure 39 compares the sludge volume achieved with the dilution method after 30 min sedimentation in the greywater and wastewater experiments.

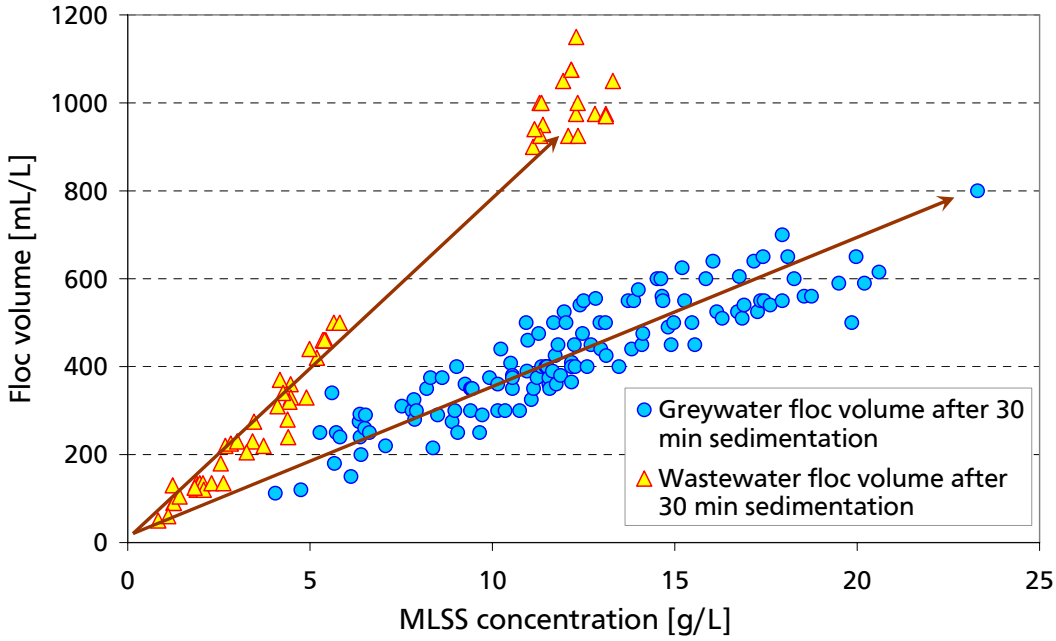


Figure 39: Relationship between sludge volume and MLSS concentration (dilution method)

Both sludges had good settlement properties. However, at a particularly *MLSS* concentration (12 g/L) the settling property of greywater sludge measured with the dilution method (~ 500 mL/L) was twice as good as that of wastewater sludge (~ 1000 mL/L). As no bulking sludge or filamentous bacteria were observed during the experiments, the different settling velocities after 30 min seemed to be the result of steric interactions or bridging between the flocs. Generally, it is assumed that these interactions increase with increasing MLSS concentration and hinder sedimentation of the sludge (Bye and Dold (1998)), which leads to non-linear settlement characteristics, as displayed in Figure 30. However, this assumption does not explain the observed differences between the greywater and the wastewater sludge at the same MLSS concentration in this study. It could be assumed that a comparison is not possible due to the different sludge origins and sludge characteristics or that the *MLSS* concentration is not an appropriate parameter to compare the results.

Another theory could be that the steric interactions depend not on the dried solid concentration but on the floc volume. The more volume is occupied by the flocs the higher the probability of collision and interaction. In this case, according to the hypothesis in Greywater Experiments Part I and II, a better correlation should be achieved if the *MLVSS* concentration is used instead of the *MLSS* concentration.

Figure 40 shows that both sludge have similar settling properties if the *MLVSS* concentration is used as a parameter for comparison.

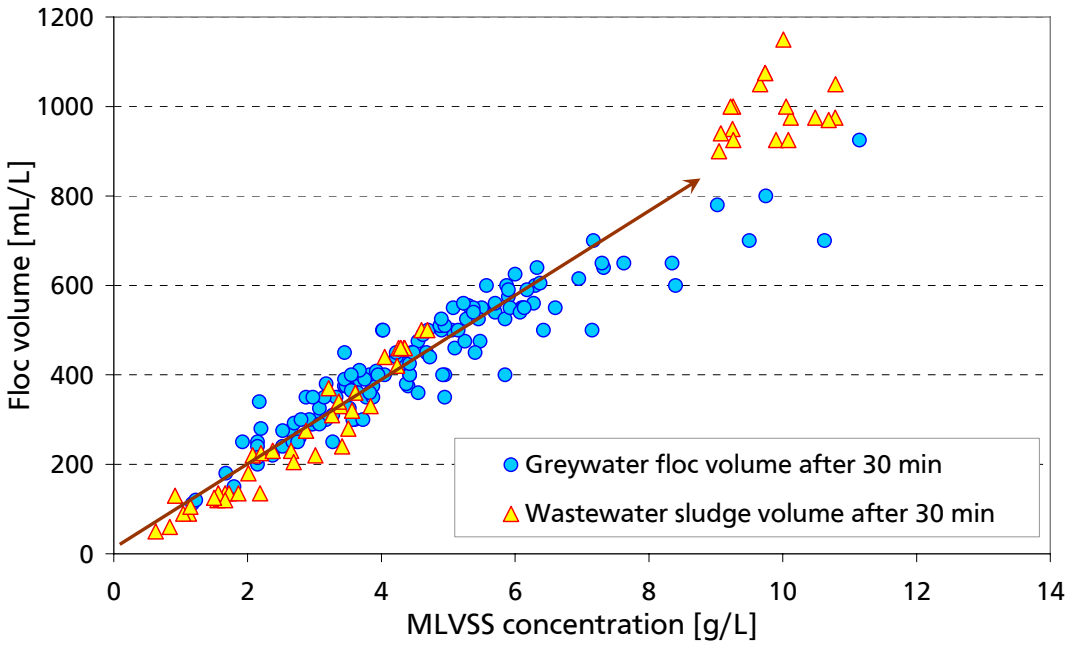


Figure 40: Relationship between different sludge volumes and MLVSS concentration (according to the dilution method)

This confirms the hypothesis about the relationship of sludge volume and the organic content of wastewater flocs and leads to the conclusion that the *MLSS* concentration is not the correct parameter to explain mechanisms that are related to floc volume phenomena, for example, the α-factor or the settlement characteristics of activated sludge.

Another purpose of this chapter was to compare the iron hydroxide results to wastewater sludge and to extend the iron hydroxide experiments to coarse bubble aeration systems. Figure 41 summarizes the results of these experiments.

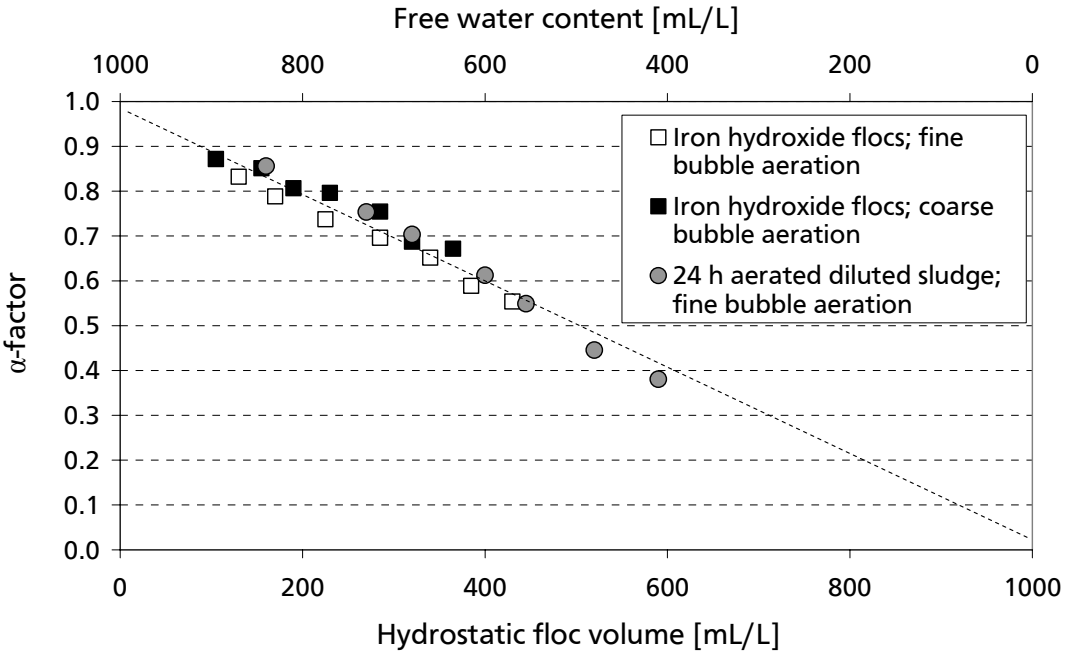


Figure 41: Hydrostatic floc volume and free water content versus α-factors from iron hydroxide and 24 h aerated diluted activated sludge experiments tested in the lab-scale column

The increase in floc volume, whether iron hydroxide or activated sludge is used, decreased the α-factor independently of the aeration device. It was shown in Greywater Experiments Part I that the increase in sludge concentration affected fine bubble and coarse bubble aeration systems in the same way. As mentioned previously, these results conflict with the current opinion that coarse bubble aeration systems generally generate higher α-factors than fine bubble aeration systems (Stenstrom and Gilbert (1981), Rosso et al. (2008)).

However, the conclusion that coarse bubble aeration systems show generally higher α-factors than fine bubble aeration systems was derived from investigations with surfactants dissolved in clean water. In this context, the observations make sense and the mechanisms were described in Section 3.2.4. However, the volume effect of the floc is different from the surface effect of surfactants in two phase systems. It shows that great care has to be taken with the transferability of observations made in dissimilar media.

In Figure 42, the data set from Figure 41 is extended to the results achieved with 24 h aerated wastewater sludge directly taken from the membrane bioreactor (not diluted). The same tendency can be observed as in iron hydroxide and diluted stabilized sludge.

Figure 43 incorporates the results of the membrane bioreactors. The same trend for 24 h aerated sludge can be observed, but the α-factors measured while the pilot plant was in operation were by trend lower.

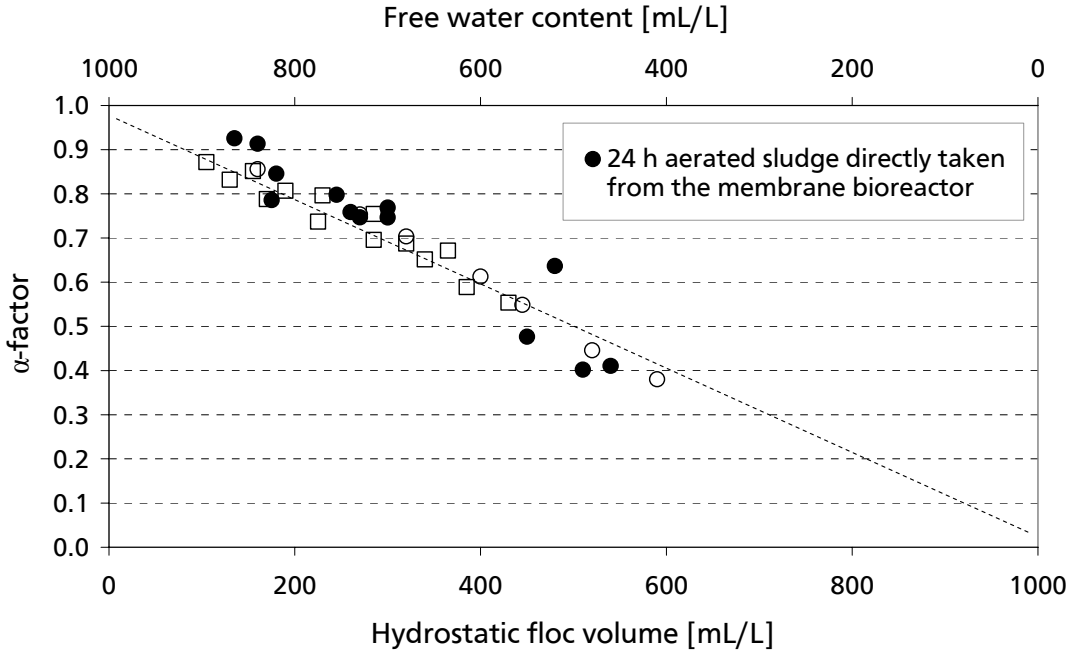


Figure 42: Hydrostatic floc volume and free water content versus α-factors including data from 24 h aerated sludge taken from the membrane bioreactor tested in the lab-scale column

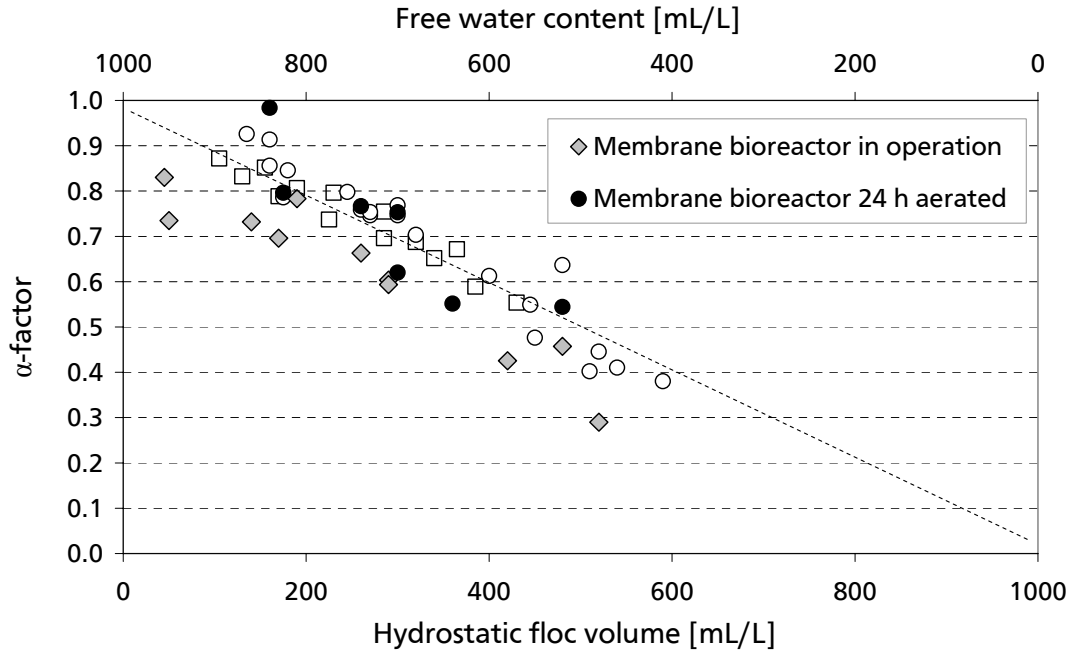


Figure 43: Hydrostatic floc volume and free water content vs. α-factors including data from the membrane bioreactor tested during operation and after 24 h of aeration

An explanation for the by trend lower α-factors may be provided by the GC-MS results. No fatty acid-like substances could be detected in the permeate and the concentration in the supernatant, if detectable, was very low, independent of whether the sludge was stabilized or in operation. In contrast long chain fatty acid-like substances adsorbed at the floc surface reduced during 24 h aeration.

It is conceivable that the lower α-factors observed during operation (compared to 24 h aerated sludge and iron hydroxide) is the result of an interaction between the floc surface and the bubble. Such behavior was already hypothesized in Greywater Experiments Part II, where lower α-factors values were determined in test series II (*SRT* 12 – 60) than in test series I (*SRT* 135 – 25).

This assumption is supported by the results of the oxygen transfer measurements with the supernatant and the permeate performed separately in the lab-scale column. Table 13 summarizes the results where GC-MS analyses were examined. Column 1 and 2 specify the corresponding experiment number and *SRT*. Columns 3, 4 and 5 present the lab-scale results, columns 6 and 7 the pilot-scale results.

Table 13: α-factors in the lab-scale experiments with wastewater ((±) standard deviation)

		Lab-scale column			Membrane bioreactor C	
No	SRT	Permeate / in operation	Supernatant/ in operation	Sludge/ 24 h aerated	Sludge 24 h aerated	Sludge/ in operation
2	2 d	0.88 (± 0.04)	0.88 (± 0.02)	1.04 (± 0.02)	-	0.73 (± 0.02)
3	8 d	1.00 (± 0.01)	1.05 (± 0.09)	0.93 (± 0.04)	-	0.70 (± 0.03)
5	19 d	0.96 (± 0.03)	0.92 (± 0.03)	0.91 (± 0.00)	0.98 (± 0.02)	0.73 (± 0.01)
7	23 d	0.97 (± 0.01)	0.99 (± 0.04)	0.79 (± 0.03)	0.80 (± 0.01)	0.78 (± 0.03)
6	36 d	0.95 (± 0.01)	0.96 (± 0.01)	0.76 (± 0.04)	0.77 (± 0.02)	0.66 (± 0.02)
4	45 d	1.06 (± 0.02)	1.02 (± 0.01)	0.77 (± 0.02)	0.75 (± 0.03)	0.60 (± 0.03)

The permeate and the supernatant, except for number 2 (*SRT* = 2 d), had only a small impact on the α-factor. In contrast, the sludge samples where the concentration of fatty acid-like substances decreased significantly during 24 h aeration show a significant increase in the α-factor. Additionally, the enhancement after 24 h aeration is always higher than could be expected with enhancement of only the liquid phase.

Similar conclusions can be drawn from the PAC experiments. When PAC was added to clean water, it had almost no effect. In raw wastewater it lead to a significant increase in the α-factor, when added to stabilized activated sludge it decreased the α-factor. Although the results are so different at first glance they serve to explain the different effects that occur in activated sludge:

- The first effect is the volume effect. The addition of 5 g/L of PAC to clean water increased the solid volume to only 24 mL/L and consequently had little effect on the α-factor. The addition of the same amount to wastewater sludge increased the hydrostatic floc volume, HFV from 75 mL/L (sludge only) to 150 mL/L (sludge + PAC) and resulted in a decrease in the α-factor from 0.93 to 0.76.
  This increase in floc volume was probably caused by the formation of smaller floc aggregates with higher specific surfaces.
- The second effect is the adsorption effect. The addition of PAC to the wastewater influent reduced the extractable amount of fatty acid-like substances significantly. In the filtered liquid phase none of these substances could be detected while the amount of

extractable substances from the unfiltered wastewater was reduced by 50 %. This lead to an increase in the α-factor from 0.33 to 0.54.
However, although no fatty acid-like substances could be detected in the liquid phase and the anionic surfactants quick test had values (0.45 mg/L) lower than in the membrane bioreactor permeate (~ 0.8 mg/L, α-factor ~ 0.98), the α-factor in this experiment was still low (0.54). This was probably caused by the following.

- The third effect is the surface effect. It occurs between the bubble and the particle surface at which loosely adsorbed material is attached. Since the addition of PAC does not lead to a degradation of the organic matter, the difference in fatty acid-like substance concentration between raw wastewater and raw wastewater with PAC was caused by adsorption. The lower amount of extractable organic matter shows that the extraction method only desorbs the lighter bound fraction. If the particles contact the hydrophobic bubble interface, this fraction interacts with the bubble surface and the oxygen transfer is reduced.

It could be argued that the dissolved *COD* concentration still present in the liquid phase after PAC addition (115 mg/L) led to the observed decrease. However Steinmetz (1996) could not find a relationship between the dissolved organic matter in activated sludge plants and the α-factor. The only significant effect from substances dissolved in the liquid phase occurred at very low *SRT* (2 d) and high *F/M* ratio.

Interesting in this context is the fact that surfactants present in detergents and fatty acid compounds of lipids overlap in their characterization and properties, especially in the range of C12 to C20 carbon chains. This close connection is not accidental, as the base products for surfactants are fatty alcohols, either from oleochemical or petrochemical sources. Today, surfactants from the oleochemical industry make up 60 % of worldwide surfactant production (see Farn (2006)). The principal raw materials are palm and coconut oil (lipids), which mainly consist of lauric acids (~70 %, C12 carbon chain) and some C14, C16 and C18 fatty acids (Condon and Matheson (1994)).

However, the composition of the fatty acid-like substances measured in the wastewater and at the floc is better matched with the fatty acid fraction present in lipids than in detergents (Dignac et al. (2000); Quemeneur and Marty (1994)). Consequently, the negative effect of these compounds adsorbed to the floc surface was probably caused by the lipid fraction.

It is commonly assumed that an increase in turbulence increases the α-factor either because the apparent viscosity of sludge or the effect of surfactants decreases with increasing turbulence (see Section 3.3.3, page 29 and Section 3.2.4, page 20). Quite the opposite was demonstrated in this study. The α-factor decreased with increasing *SGV*. The effect seemed to amplify as the sludge volume increases and the iron hydroxide experiments showed clearly that this effect was not caused by respiration, surfactants or any other biological effect. At elevated sludge volume it resulted in a non-linear relationship of k_La versus *SGV* and can be attributed to the change from homogenous to transition flow regime caused by coalescence in fine bubble aeration systems (Section 3.2.3.2). Beside coalescence, it is also conceivable that the diffusivity of the floc may have contributed to this effect. Sun and Furusaki (1989) showed that the k_La value that accounts for intraparticle diffusion is higher than the measured one. This effect increases with increasing floc volume and would be independent from the

bubble size produced. Comparison of the oxygen transfer measurement results indicates that this effect is induced by diffusion not turbulence. In the experiments with high k_La values (lab-scale column with fine bubble aeration), the difference in α-factor at elevated sludge concentration was high (standard deviation up to 25%), while in the experiments with lower k_La values (lab-scale column with course bubble aeration, membrane bioreactor experiments) the differences were low (standard deviation ~ 5%). If turbulence caused this effect, big differences should also have occurred in the lab-scale column equipped with coarse bubble aeration. This was not the case. However, further investigations are required to get a better insight into this phenomenon.

Finally, the results suggest that the HFV value may serve for comparison of α-factors from different origins. In contrast to the *MLSS* and *MLVSS* concentrations, it describes a sludge property. Contrasted with viscosity, it is closer to the microscopic reality since it does not merge floc and liquid phase. It opens a wider field of probable mechanisms comparable to the solid holdup as discussed in chemical engineering.

5.3.7 Conclusions

a) Better correlation of the α-factors in this study and in other studies is achieved if the *MLVSS* concentration is used as a basis for comparison.

b) The same observation was made with the settling characteristics of sludge achieved after 30 min. This supports the hypothesis that the *MLVSS* concentration better reproduces the free water content and the floc volume than the *MLSS* concentration.

c) Using the hydrostatic sludge volume as a basis for comparison of wastewater and iron hydroxide α-factors, similar behavior to the depletion in oxygen transfer with increasing floc volume is observed. Consequently, the floc volume and the free water content are the main drivers for α-factor depletion with increasing suspended solids concentration.

d) Experiments with the permeate, the supernatant and PAC added to raw wastewater, stabilized sludge and clean water in the lab-scale column, support the assumption that substances adsorbed to the solid surface interact with the bubble surface and reduce oxygen transfer in activated sludge in additional to the floc volume effect.

e) Fatty acids or surfactants dissolved in the liquid phase played only a minor role in the depletion of the α-factors.

f) Coarse bubble and fine bubble aeration systems have the same dependency on the effect of the floc volume. However, the microscopic effect that led to this result still remains unsolved.

5.4 Oxygen transfer phenomena – new insights

With the findings from Sections 5.1 to 5.3 and the results of other investigations, it is possible to paint an overall picture of how oxygen transfer is influenced in activated sludge systems equipped with submerged aeration systems.

5.4.1 Influence of the solid phase

The properties of the solid phase, especially its organic fraction, govern oxygen transfer in activated sludge. It is responsible for the floc volume in the system, and determines the grade of degradation and adsorption, therefore controlling the amount of substances left in the liquid phase. Last but not least, it interacts actively with the bubble interface and thus influences its behavior.

5.4.1.1 Free water content and floc volume (solid holdup)

As quoted previously, the majority of the sludge volume is made up of flocs with a diameter bigger than 140 µm (Schmid et al. (2003)). If the total volume of a suspension is not changed, the increase in floc volume occurs with a decrease in the free water content. In this case, the following phenomena may influence the oxygen transfer (summarized from Section 3.3.2):

a) The increased floc volume decreases the interfacial area between the bubble and the liquid phase, since it attaches to the bubble surface and hinders the transfer to the liquid phase

b) The attachment of small, hydrophobic flocs may favor the coalescence tendency

c) Turbulence of the bubble wake is diminished, caused by accumulation of the flocs in the wake area

d) With increasing floc number, the possibility of collision during bubble formation at the orifices increases, which reduces the bubble formation frequency and leads to bigger bubbles at the orifice

e) The decrease in the free water content leads to an increase in gas holdup related to the liquid phase at the same air flow rate. This shifts the critical superficial gas velocity (*SGV)* velocity, which is responsible for the change from the homogenous flow regime to the heterogeneous flow regime, to lower values

f) The increased floc volume also increases the probability of collision between the flocs themselves and increases the apparent viscosity. This again leads to an decrease in the liquid velocity at the same air flow rate, which results in bigger bubble formation at the orifice and enhances the probability of bubble coalescence

All effects decrease the oxygen transfer coefficient k_La in activated sludge. Since the suppression of the α-factor for fine bubble and coarse bubble aeration systems were similar, and bubble formation and bubble rise characteristics of coarse bubbles are not affected by the liquid properties, only two phenomena remain that could explain the similar behavior. One is the reduction of turbulence in the bubble wake area, the other describes the suppression of

the oxygen transfer from the bubble to the liquid phase. However, further investigations are required to determine which mechanism rules this phenomenon.

A second effect of the floc volume is related to the flow regime in fine bubble aeration systems. At hydrostatic floc volumes (HFV) higher than 500 mL/L, the relationship between k_La and *SGV* changed from linear to non-linear, which indicates a shift of the flow regime from homogeneous to heterogeneous, caused by coalescence phenomena, as explained in Section 3.2.3.2. In the experiments, the critical *SGV* was always lower than 4 cm/s and so a homogeneous flow regime was expected for fine bubble aeration systems. However, an increase in solid holdup shifts the critical *SGV* to lower values (Section 3.3.2). It is conceivable that the same effect is achieved with an increase in floc volume. It may explain why the α-factor at higher *SGV* was lower than at lower *SGV* and supports the hypothesis that activated sludge flocs favor coalescence. This phenomenon is fundamentally different from the effect of dissolved surfactants on oxygen transfer, as described in Section 3.2.4, where an increase in *SGV* leads to higher α-factors and coarse bubble aeration systems are less affected than fine bubble aeration systems.

5.4.1.2 Adsorption, degradation and surface phenomena

According to Raunkjær et al. (1994), the largest fraction of the wastewater influent consists of macromolecules, such as proteins, carbohydrates, and lipids. To be metabolized, these molecules must be in contact with bacteria, which is ensured by convection to the floc, adsorption at the floc surface, diffusive transport through the floc, extracellular enzymatic degradation at the bacterial surface, and active transport from the outer membrane into the cytoplasm. The overall reaction rate, which includes adsorption, hydrolysis, and synthesis, is limited by the extracellular enzymatic hydrolyses (Novak et al. (1995)). The adsorption process instead is a fast process which reaches equilibrium after a few minutes or a few hours, depending on the fraction property (colloidal/soluble; see Guellil et al. (2001)), and is favored by the long-range hydrophobic attraction between hydrocarbon surfaces in water, which is 10 - 100 times larger than any van der Waals force (Christenson and Claesson (2001)).

For carbon elimination only, the activated sludge process requires an *SRT* around 2 - 4 d. Phan (2005) showed that under these circumstances the adsorption capacity of activated sludge is almost exhausted, which indicates that a significant amount of organics is not degraded but removed by adsorption from the sludge. GC-MS measurements showed that biodegradable substances had been adsorbed at low *SRT* (2 d) to the floc surface. Both C14 and C15 fatty acid-like substances could be detected at the sludge surface, but none were found in the supernatant or the permeate.

At such low *SRT* in conventional activated sludge plants (Section 3.3.3.2, Figure 13) as well as in this study, the α-factor is significantly lower than could be expected by the floc volume alone. Since significant amounts of fatty acid-like substances could not be detected in the permeate or the supernatant, and the oxygen transfer test in the lab-scale column only showed a small effect on the α-factor, it is very likely that this effect is caused by the interaction of the highly loaded floc surface and the bubble. As the floc adsorption capacity increases, the organic matter can exchange between the floc and the bubble surface, a process

that is favored by the hydrophobic properties of both the bubble and the floc. This interaction may reduce the diffusivity of the bubble and make the surface more rigid, as is reported to be the case in dissolved surfactants (Section 3.2.4).

With increasing *SRT*, the degradation enhances and the easily degradable substances are removed from the floc surface (Table 22 - Table 28, Appendix, Section 11.13, page 135). The total floc volume increases, caused by an increase in reactor volume or *MLSS* concentration. Both effects raise the floc surface available for adsorption, which also influences hardly/slowly biodegradable substances, such as humic compounds or long chain fatty acids, which are highly adsorbable. Humic acids are frequently found in the EPS matrix of activated sludge (Frolund et al. (1995)), which shows that, beside adsorption at the floc surface, these compounds also incorporate/absorb into the floc matrix.

To estimate the adsorption properties of substances, the water-octanol partition coefficient K_{ow} is used. It describes the fraction of a substance in a two-phase mixture that is composed of water and octanol. The higher the K_{ow} value the better the substance attracts to the organic phase. Byrns (2001) and Struijs et al. (1991) developed a model for xenobiotic organic compounds based on the physical and chemical properties. They conclude that substances with higher log K_{ow} values than 4 are mainly removed by adsorption in conventional activated sludge plants whereas substances with lower K_{ow} values are removed by biodegradation.

Similar results emerged from the GC-MS analyses here. In the greywater experiments (see Appendix, Section 11.12, page 134) C12 fatty acid-like substances, in this case, mainly represented by SDS (log K_{ow} SDS ~ 1.6), could not be detected in the permeate, supernatant and floc surface, even at an *SRT* of 12 d and high influent concentration (45 mg/L). This could also be expected from the literature data on the degradation of these compounds (White and Russell (1993), Knepper and Eichhorn (2006)).

However, C14 fatty acids (log K_{ow} myristoleic acid ~ 5.2) were still adsorbed by the greywater and wastewater sludge at *SRT* of 12 d. Finally, long chain fatty acids (C16/C18), such as oleic acid, palmitoleic acid and linoleic acids, with log K_{ow} values higher than 6 were adsorbed at the floc surface even at high *SRT* and could only be reduced in their concentration when the sludge was aerated for 24 h. Besides a degradation process, it is also conceivable that these substances were eliminated via adsorption into the bubble, forming a foam layer at the reactor superficies.

In summary, with decreasing *SRT* the impact of adsorbed organic matter on the oxygen transfer increases and with increasing *SRT* the adsorption capacity of sludge increases. This also explains the observations made by Steinmetz (1996) on shock loads in activated sludge plants operating at low and high *SRT* and their impact on the α-factors. If the shock loads are applied to wastewater plants with an *SRT* higher than 30 d (high adsorption capacity), no change in the α-factors is observed. If the shock loads are applied to treatment plants operating at lower *SRT* (4 - 12 d, no/low adsorption capacity), a decrease in the α-factors is observed with every shock load applied.

Other operational parameters that are indirectly related to the *SRT* and affect the adsorption behavior of activated sludge are the recirculation flow and the daily variation of the *COD*

load. Usually in conventionally activated sludge plants with only carbon removal or nitrification (*SRT* < 8 d) the quotient of recirculation and the influent flow is around one or lower, while denitrification plants (*SRT* ~ 11 d) include an internal recirculation flow to achieve sufficient denitrification. Since the influent and recirculation flow are usually not homogeneously distributed over the whole reactor volume but mixed in a pre-chamber before entering the biological reactor, the single floc is exposed to different *COD* loads which vary during the day.

Pujol and Canler (1992) observed a maximum adsorption capacity of activated sludge of 60 mg *COD*/g *MLSS* while Guellil et al. (2001) reports a range from 40 to 100 mg *COD*/g *MLSS*. With these observations and the calculations made in the Appendix, Section 11.18, page 148 in activated sludge plants with carbon removal and nitrification, the adsorption capacity of the sludge will be exhausted (up to 140 mg *COD*/g *MLSS*), while in denitrification plants it is mostly lower (up to 45 mg *COD*/g *MLSS*). As stated previously, a higher floc load leads to depression in the α-factor, since the loosely bound organic matter interacts with the bubble surface. Especially in plug flow reactors with increasing distance from the influent and the consequent increase in degradation this effect reduces and an increase in α-factor can be observed (EPA (1989)).

5.4.2 Influence of the liquid phase and the role of surfactants

The liquid phase reflects the characteristics of the wastewater influent. Generally, the wastewater influent strongly decreases the α-factor, as demonstrated by Kayser (1967), Steinmetz (1996) and in this study (Section 5.3.3). This effect is explained by the interaction of dissolved organic surfactants present in the liquid phase with the bubble. However, the GC-MS results demonstrated that even in the influent the biggest fraction of fatty acid-like substances, including surfactants, are already adsorbed to particulate matter, which is in line with the observation made by Quemeneur and Marty (1994). Additionally, the experiments with the permeate showed only a minor impact on the α-factor, except for an *SRT* of 2 d. A similar result was obtain by Kayser (1967) with the effluent of a wastewater treatment plant. This leads to the assumption that dissolved substances play only a minor role in depletion of the α-factor in municipal wastewater treatment plants. It additionally explains why Steinmetz (1996) could not find a dependency of the α-factor with increasing DOC concentration in wastewater sludge.

Concerning the question of which substances present in the influent and attached to particulate matter actually decrease the α-factor, it can be assumed that the lipid fraction plays a more important role than surfactants present in detergents. The majority of lipids in wastewater are triacylglyerides that cannot be consumed directly by the bacteria in activated sludge and have to be hydrolyzed first (Dueholm et al. (2001)). The hydrolyzed byproducts are again long chain fatty acids (C16/C18 carbon chain length), that occasionally could be detected in the supernatant and were always detectable at the floc surface. In contrast, the commonly used surfactants in detergents (SDS, C12 carbon chain length) could not be detected in the effluent, the supernatant or at the floc surface even though their concentration was high, especially in the greywater experiments (~ 45 mg/L).

5.4.3 The correlation of floc volume and SRT in respect to the α-factor

To visualize the overall dependency of the α-factor on the floc volume (solid holdup) and the *SRT*, which incorporates the adsorption and the degradation properties of activated sludge, a three-dimensional plot is required (Figure 44). It is based upon the calculations presented in the Appendix Section 11.19 page 150 and follows the equation

$$\alpha - factor = 0.51 - 0.062 \cdot MLVSS + 0.019 \cdot SRT \pm 0.114 \qquad (5\text{-}1)$$

Instead of the HFV, the *MLVSS* concentration was chosen to represent the floc volume to make the relationship comparable to already existent data.

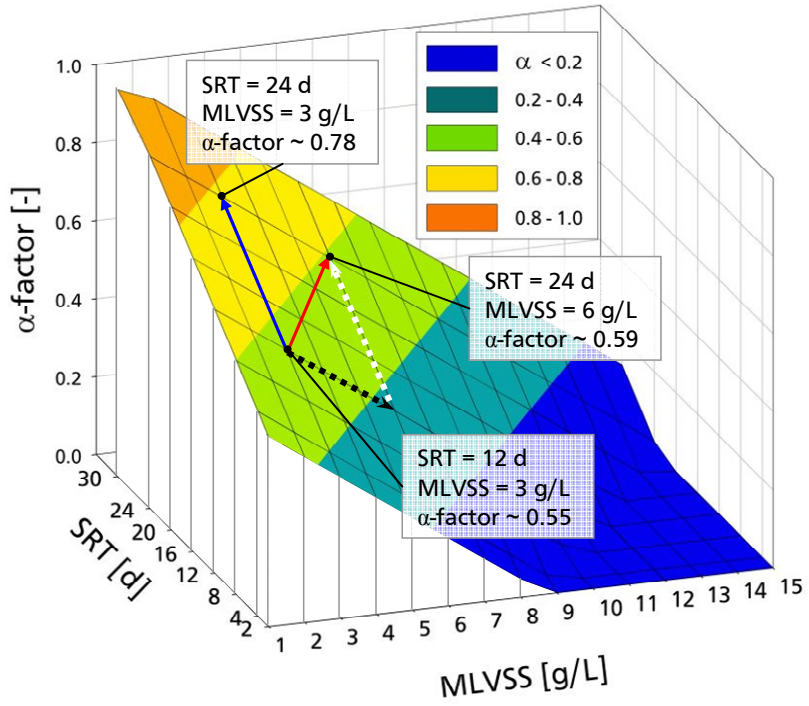


Figure 44: Development of the α-factor as a function of SRT and MLVSS concentration

In membrane bioreactors, the *SRT* can be decoupled from the reactor volume because the *MLSS* concentration is freely selectable. On the one hand, increasing the *SRT* by increasing the *MLVSS* concentration leads to an increase in floc volume and a subsequent decrease in the α-factor (Figure 44, dashed black arrow). On the other hand, it improves the degradation and adsorption process, which leads to enhancement of the α-factor (Figure 44, dashed white arrow). The actual α-factor includes both effects (Figure 44, red arrow).

Other investigators (EPA (1989), Rosso et al. (2008), Gillot and Heduit (2008)) observed that α-factors increase continuously with increasing *SRT*. These observations were made in conventional activated sludge plants without considering the effects of free water content, *MLVSS* concentration, or floc volume.

In a conventional activated sludge plant, higher *SRT* is achieved by increasing the reactor volume for a narrow range of *MLSS* concentrations. In this case, the impact of the floc volume on the α-factor remains relatively constant, whereas the negative influence of substances that are adsorbed at the floc surface decreases steadily because the degradation

process improves and the available floc surface for adsorption increases with increasing *SRT* (Figure 44, blue arrow).

For selected *MLVSS* concentrations Figure 44 can simplified as follows:

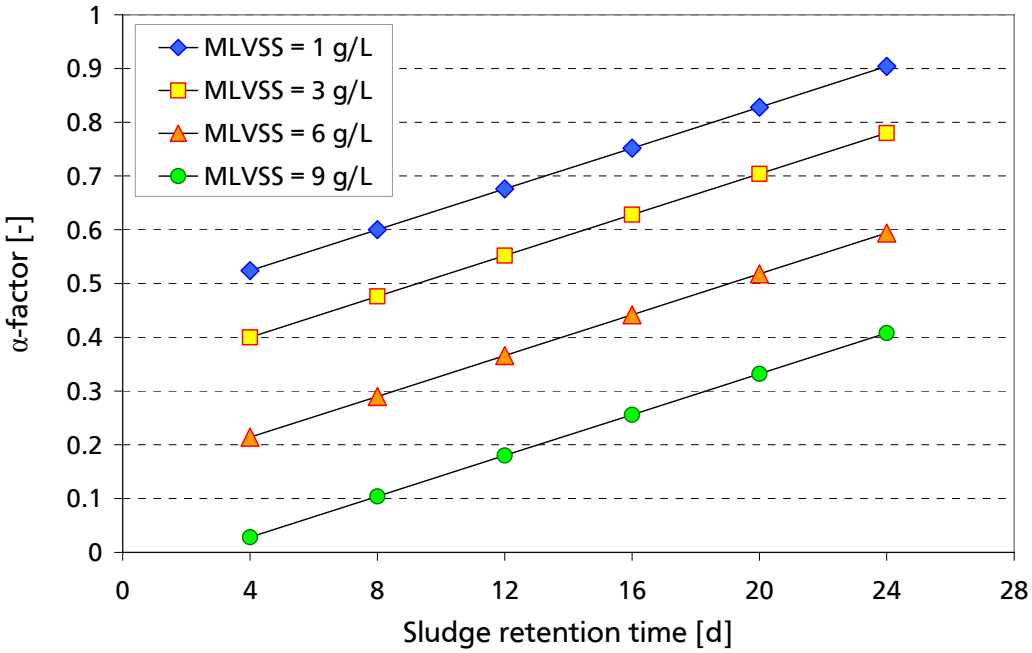


Figure 45: Simplification of α-factor dependency on SRT and MLVSS concentration

As in Figure 44, with increasing *MLVSS* concentration the α-factor declines, while with increasing *SRT* the α-factor increases. Although both figures help to understand the interdependencies of α-factor, floc volume and *SRT* and may be used to estimate the development of the α-factor, an exact calculation is still not possible. For this purpose, the range of data in the database is still too high and more data, especially on the relationship between α-factor and *SRT* (which currently does not consider the floc volume), is required.

5.5 Consequences for practice

Practical recommendations can be derived after the effects of activated sludge on submerged aeration systems have been demonstrated. For a high α-factor in fine bubble aeration systems, low specific diffuser airflow rates, low suspended solids concentration (low floc volume) and high *SRT* should be chosen. In practice, this can be implemented by minimizing the organic load, utilizing the maximum reactor volume or decreasing the suspended solids concentration.

However, these actions compete with the stable operation of the plant. Minimizing the *COD* load by having a longer sedimentation time in the preliminary sedimentation may lead to deficiency in the organic substrate needed for stable denitrification. Increasing the *SRT* throughout higher reactor volumes requires more space for construction. Additionally, the energy content in activated sludge decreases with increasing *SRT*, affecting the gas production of the digester.

Additionally the *MLVSS* concentration (floc volume) is a parameter that cannot currently be determined before the operation of a wastewater treatment plant starts. Consequently, an exact prediction of the α-factor is still not possible. However, the relationship between α-factor, *SRT* and *MLVSS* concentration (Figure 44) enables comparison to the current procedure. The required standard oxygen transfer rate (*SOTR*) can then be determined and related to experiences in wastewater technology. The data and assumptions for the following calculations are summarized in the Appendix (Section 11.2, page 118).

5.5.1 Plant design

The α-factor has the biggest impact on the required *SOTR* in an activated sludge plant. The uncertainty in pre-determining α-factors lead to the practice, at least in Germany, that the α-factor value is specified by the client for the design of a wastewater treatment plant (DIN 19569-3, DIN (2002)). However, in many cases, the client is less qualified to specify the α-factor than the contractor. Thus, a fixed α-factor of 0.6 for conventional activated sludge plants or 0.5 for membrane bioreactor systems is often predefined.

This procedure led to the current opinion that simultaneous aerobic stabilization (*SRT* > 25 d at 12°C) requires the highest *SOTR* of all activated sludge processes. This assumption is made because the oxygen uptake rate (*OUR*) by the bacteria (for carbon removal) increases with increasing *SRT*.

If a fixed α-factor is used in the *SOTR* calculation at constant temperature (here 12°C) and *MLSS* concentration (3.75 g/L), *SOTR* increases steadily with increasing *SRT* (Figure 46). Applying a variable α-factor according to Equation 11-29 (Appendix, Section 11.19, page 150), at *SRT* higher than 4 d the increase of α-factor overcompensates the increase in *OUR* by better oxygen transfer to the sludge. Thus, aerobic stabilization plants should show the lowest required *SOTR* (Figure 46).

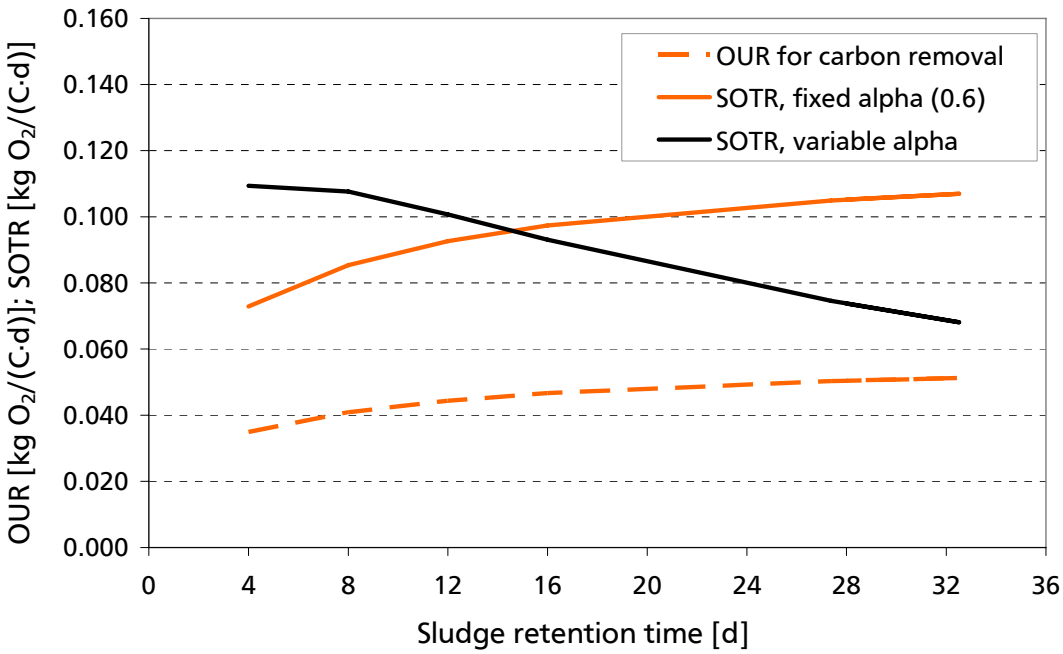


Figure 46: Comparison of oxygen uptake rate (OUR) for carbon removal, SOTR calculation with fixed and variable α-factor (per capita)

However, the final required *SOTR* depends not only on the organic load, but also on the ammonium load and the plant design. At *SRT*s higher than 4 d bacteria accumulate in the reactor that oxidize ammonium, which leads to an increase in the required *SOTR*. If a pre-denitrification unit is installed, the required *SOTR* decreases again, since denitrification reduces the organic load to the aeration basin. Last but not least, aerobic stabilization plants (*SRT* > 25 d at 12°C) do not have a preliminary sedimentation in contrast to other plant designs and thus treat a higher influent load (~ 50 % higher organic load + ~ 10 % higher nitrogen load). Incorporating these assumptions into the calculations of the required *SOTR* leads to the results pictured in Figure 47.

Using a fixed α-factor of 0.6, the required *SOTR* turns out to be lower than using a flexible α-factor, except for the case of aerobic stabilization without primary treatment. In this case, the required *SOTR* with a fixed α-factor is about 43 % higher than when calculated with a flexible α-factor and about the same amount higher compared to the denitrification plant. Applying a flexible α-factor for aerobic stabilization, the required *SOTR* is equal to that of the denitrification plant.

To verify which method is closer to reality, a comparison to values received in practice is required. However, data is lacking because the required α-factor is seldom determined in practice. However, since the required *SOTR* is directly related to the energy consumption of the blowers, which, as quoted previously, is responsible for about 60 % of the total energy demand of an activated sludge plant, estimation can be made by comparing energy consumptions.

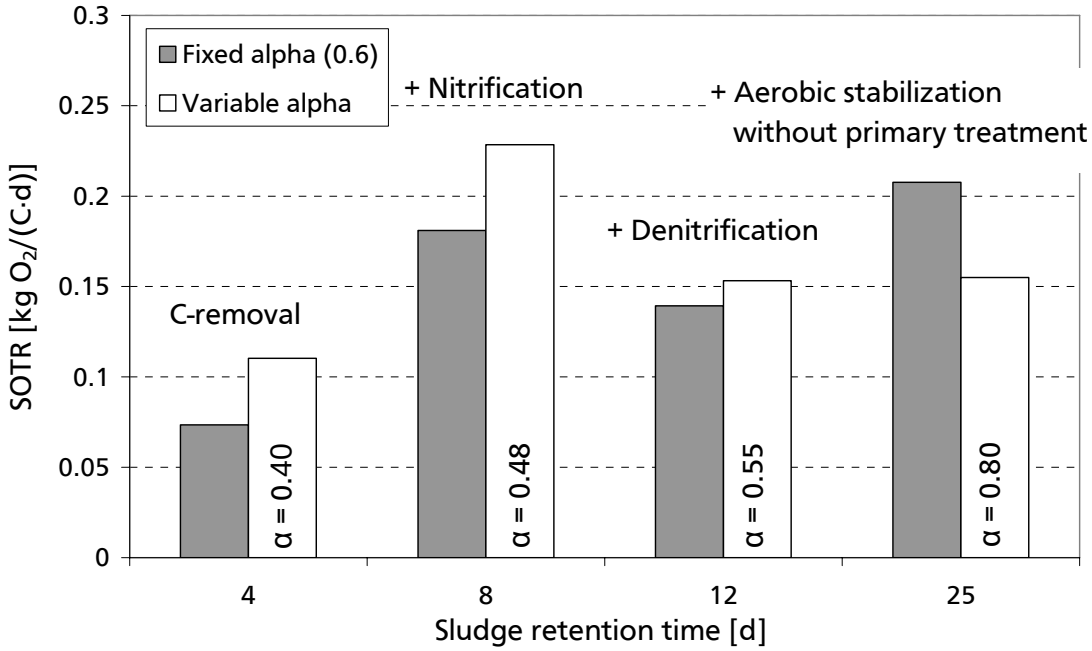


Figure 47: Comparison of SOTR (per capita) calculated with fixed and variable α-factors for activated sludge designs, as constructed in practice

LFU (1998) investigated 143 activated sludge plants that had similar population loads (5,001 – 10,000 PT) with and without aerobic stabilization. Although operated without preliminary sedimentation, the aerobic stabilization plants (n = 80) had similar energy consumption per capita (40.9 kWh/(C·a)) to other activated sludge plants (n = 65, 40.7 kWh/(C·a)). LFU (1998) reports that this result is noteworthy for two reasons; first, because the theoretically required *SOTR* (calculated according to the old concept of the fixed α-factor) should be significantly higher than for the other activated sludge processes, including preliminary sedimentation, and second, because aerobic stabilization plants have better overall *COD* and nitrogen removal. No explanation could be given for these results. However, using the new approach of a variable α-factor, this result is explainable. The enhanced α-factor at elevated *SRT* compensates the better degradation, the increased *OUR* of the bacteria and the increased load (no preliminary sedimentation). Consequently, in terms of aeration and currently available data, aerobic stabilization is the most efficient activated sludge process when related to the degraded/oxidized load (Figure 48).

The results of Figure 47 indicate that using a fixed α-factor of 0.6 for plants with nitrification and carbon removal underestimates the required *SOTR*. In practice, this is usually not observed because the installed normalized airflow rate is calculated according to the hourly peak load, which incorporates a security factor, and many wastewater treatment plants operate below capacity.

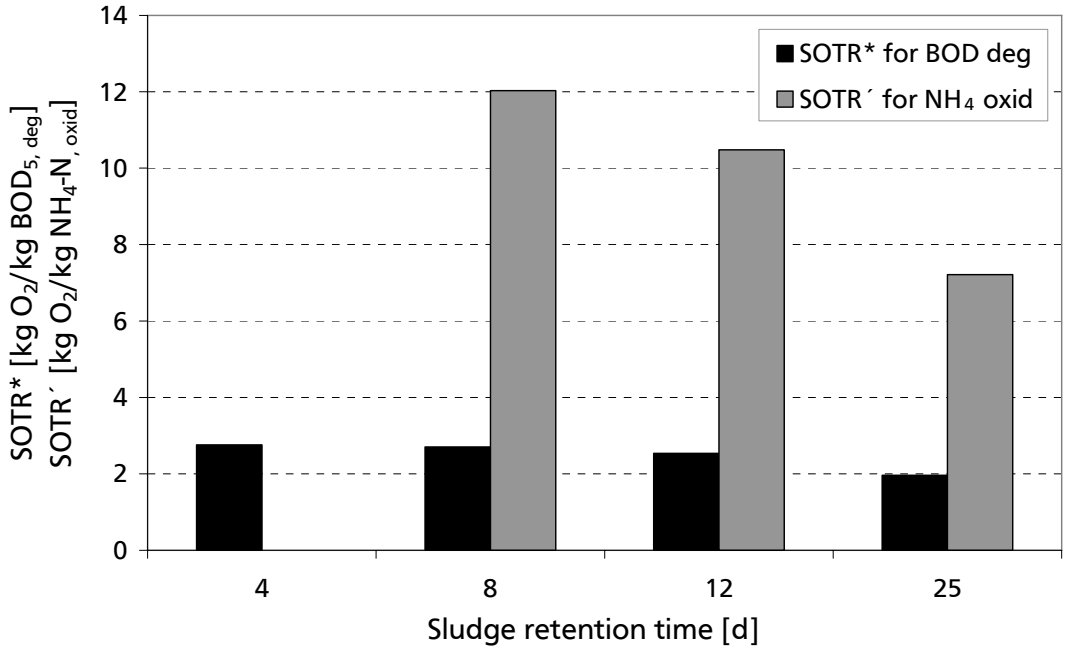


Figure 48: specific SOTR*,` for the BOD and NH_4 load entering the aeration basin at different SRT

5.5.2 Plant operation

Activated sludge plants are designed to cope with a minimum temperature during the winter period. Consequently, during summer the operator has the following options:

1. No seasonal adaptation: The aerated reactor volume and the sludge concentration are kept constant. The *SRT* will increase, caused by faster bacteria metabolism, which leads to a higher respiration rate, which lowers the excess sludge production.
2. Applying seasonal adaptation by reducing the *SRT* to the minimum required at the current temperature. Here, the operator has two choices:
   a) Reduce the reactor volume
   b) Decrease the sludge concentration.

Generally, it is assumed that reducing *SRT* is the best choice, since at lower *SRT* the respiration rate is lower and so oxygen demand reduces. However, this assumption does not take into account the change in α-factor at different *SRT* and floc volume. Figure 49, Figure 50 and Figure 51 summarize the calculation of the SORT using a variable α-factor for three different wastewater treatment plant designs:

- Advanced nutrient removal
- Aerobic stabilization and
- Membrane bioreactors

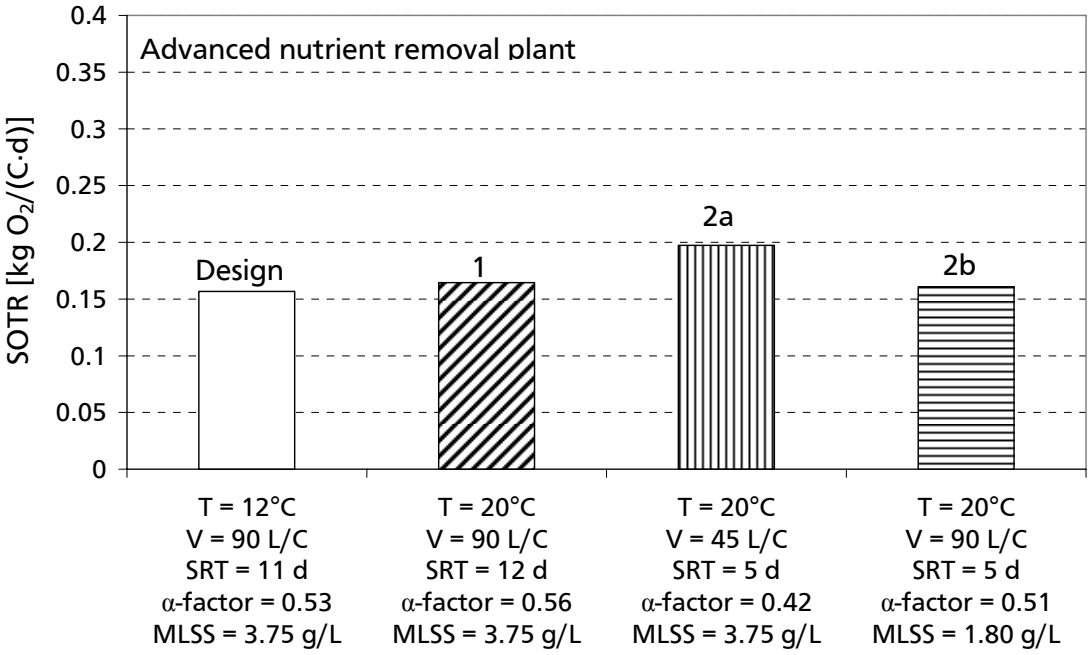


Figure 49: SOTR calculation (per capita) for a conventional activated sludge plant with advanced nutrient removal

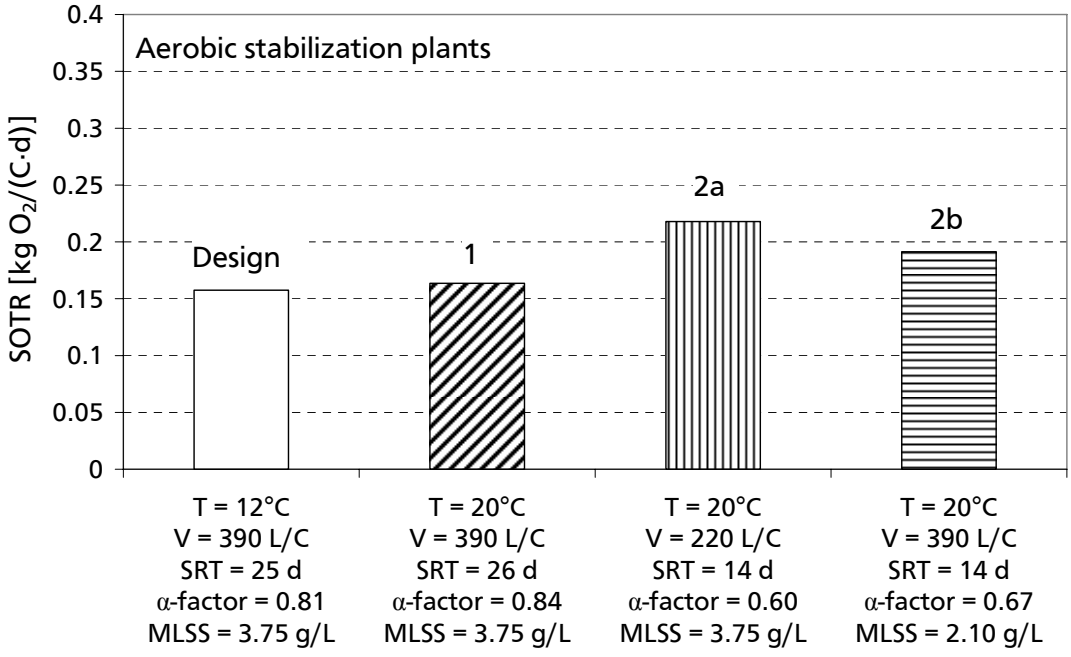


Figure 50: SOTR calculation (per capita) for an aerobic stabilization plant

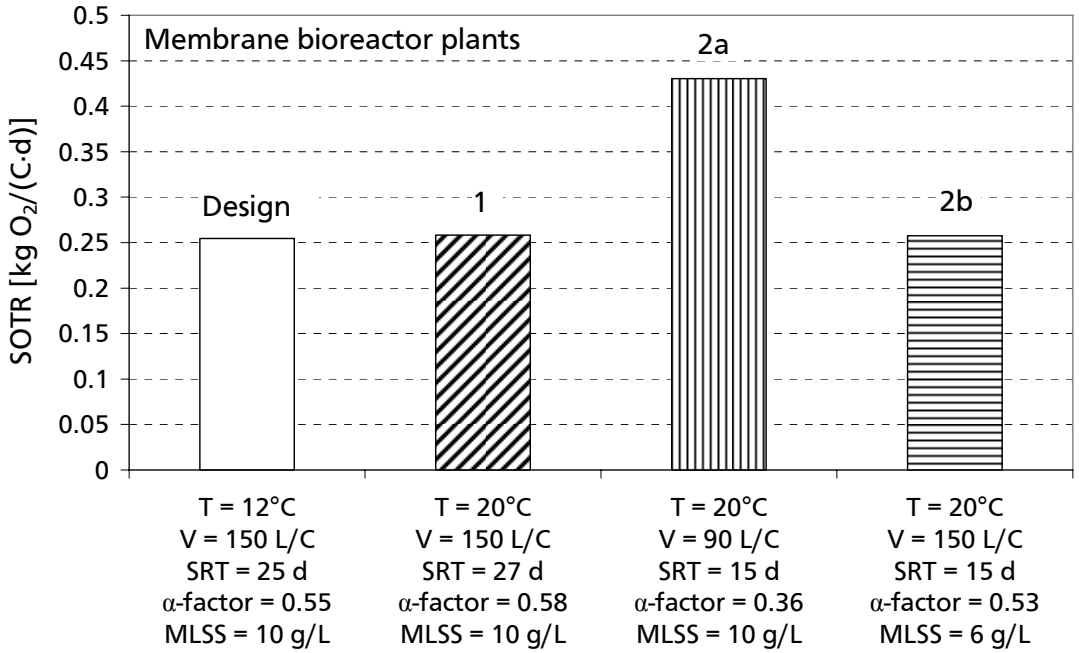


Figure 51: SOTR calculation (per capita) for a membrane bioreactor plant

In all cases, the required *SOTR* is highest if *SRT* is reduced by reducing the reactor volume and keeping the *MLSS* concentration constant (2a). No seasonal adaption (1) and reducing the *SRT* by lowering the *MLSS* concentration (2b) lead to similar *SOTR* values. Which of these options is the best choice cannot currently be determined. Only if the degradation and adsorption behavior of activated sludge for aerobic stabilization at an *SRT* of 15 d and 20°C is similar to an *SRT* of 25 d and 12°C (as is assumed by calculating the minimum required *SRT* to meet the German standard, ATV A 131 (ATV-DVWK (2000)), option 2b should lead to lower *SOTR* values than for option 1. However, this is highly speculative since the theoretically derived *SRT* calculations are based only on the growth rate of bacteria and its dependency on temperature. Adsorption and degradation phenomena are not considered in this calculation.

The generally higher required *SOTR* during summer (compared to the winter period) observed in all figures is the result of an 67 % increase in temperature (12 → 20°C), which lowers the oxygen saturation concentration from 10.78 mg/L at 12°C to 9.09 mg/L at 20°C, which again reduces the concentration gradient about 15 % and therefore increases the required *SOTR*.

6 Summary

Oxygen supply is still the biggest energy consumer in the activated sludge process (~ 60 %, Roth (1998)). The α-factor, i.e. the relationship of wastewater to clean water oxygen transfer coefficient, has the greatest impact on the required standard oxygen transfer rate (*SOTR*), which is the key parameter in the design of diffused aeration systems in an activated sludge plant.

The major objective of this dissertation is to introduce the complex interdependency between solid, liquid and gaseous phases in oxygen transfer in activated sludge systems and to study the impact of activated sludge on oxygen transfer. Additionally, the effect of surfactants on oxygen transfer is investigated and a method is developed to determine the floc volume of activated sludge. The α-factor is chosen to enable comparison of oxygen transfer coefficients. Three sets of investigations are performed:

a) Greywater Experiments Part I investigates the impact of coarse and fine bubble aeration systems on the α-factor at different mixed liquid suspended solids (*MLSS*) concentrations, using artificial greywater with a high anionic surfactants concentration (70 mg/L). Although different reactor configurations are used, the α-factor decreases in the same way, independent of the chosen aeration system. A comparison with other data using the preferred *MLSS* concentration shows a wide spread. However, a much better correlation is achieved by choosing the mixed liquid volatile suspended solids (*MLVSS*) concentration instead of the *MLSS* concentration.
   The experiments reveal that the impact of commercial surfactants on oxygen transfer in an adapted, completely mixed, activated sludge system operating at high sludge retention times (> 25 d) is negligible, despite high influent concentration (70 mg/L). The liquid phase (effluent of the membrane bioreactor) has the same oxygen transfer coefficient as clean water (α-factor = 1). It is hypothesized that neither viscosity nor surfactants are responsible for the decrease in oxygen transfer but the free water content and the floc volume of the suspension.

b) In Greywater Experiments Part II, a method is developed which approximates the floc volume (hydrostatic floc volume, HFV). The impact of the floc volume is demonstrated using iron hydroxide flocs. The α-factor decreases linearly with increasing floc volume and decreasing free water content, at least up to a floc volume of 500 mL/L. Biological or adsorption processes are thus not responsible for this phenomenon.
   By selectively changing the *SRT*, the effects of *MLSS* and *MLVSS* concentrations is demonstrated. The experiments reveal that the suspended solids concentration in the influent and the degradation/adsorption processes and/or the growth of the biomass at different *SRT*s cause the wide spread of the α-factor values observed to date in practice. As in Greywater Experiments Part I, better correlation with the α-factor is achieved if the *MLVSS* concentration instead of the *MLSS* concentration is used.
   Although the *SRT* is reduced (~ 12 d) and the surfactant concentration in the influent is high (~ 60 mg/L), dissolved substances (membrane bioreactor effluent) have no impact on the α-factor. It seems that slowly degradable surfactants (long chain fatty acids)

adsorbed to the floc surface interact with the bubble and lead to a lower α-factor than expected with only the floc volume.

c) The third set of experiments uses real wastewater. α-factors from greywater experiments and wastewater experiments again correlate better if the *MLVSS* concentration is used instead of the *MLSS* concentration.
Experiments with 24 h aerated activated sludge and iron hydroxide with coarse and fine bubble aeration show the same decline in the α-factor when the HFV is used for comparison. Consequently, the results obtained during Greywater Experiments Part I may be explained by the influence of the floc volume, which affects the α-factor in the same way, independent of whether coarse or fine bubble aeration systems are used. Furthermore, the majority of surfactants in the influent is already adsorbed to suspended solids. Experiments using powdered activated carbon (PAC) and investigations with the membrane bioreactor in operation strengthen the hypothesis that surfactants adsorbed to the floc and not dissolved in the liquid phase interact with the hydrophobic bubble surface.
Dissolved substances (membrane bioreactor effluent) only have a significant impact on oxygen transfer at *SRT* less than 8 days (here 2 d).
Generally, with increasing airflow, the oxygen transfer coefficient increases but the α-factor decreases. This phenomenon is more pronounced at higher oxygen transfer coefficients and floc volumes, and leads to a decrease in oxygen transfer efficiency.
The comparison of sludge settlement characteristics performed with the dilution method after 30 min confirms that the floc volume correlates better with the *MLVSS*. When the *MLVSS* concentration is used instead of the *MLSS* concentration, a good correlation is achieved and the phenomena can be explained by steric interactions (hindered sedimentation).

Knowing the different effect of floc volume and *SRT* on the α-factor a comprehensive interrelationship can be established. Thus, with increasing *SRT* at a constant floc volume, the α-factor increases up to an *SRT* of 30 d, while at a constant *SRT*, with increasing floc volume, the α-factor decreases linearly, at least up to a floc volume of 500 mL/L (~12 g/L *MLVSS*). The overall effect can be approximated by the following equation:

$$\alpha - factor = 0.51 - 0.062 \cdot MLVSS + 0.019 \cdot SRT \pm 0.114$$

with

MLVSS	[g/L]	mixed liquid volatile suspended solids concentration [1 - 12 g/L]
SRT	[d]	sludge retention time [1 - 30 d]

An exact prediction of the α-factor with this equation is still not possible because of the spread of the data and the difficulty of predicting the *MLVSS* concentration in activated sludge plants before operation commences.

However, the equation can be used to compare the new findings with the current procedure (fixed α-factor). The enhancement of the α-factor with increasing *SRT* overcompensates for the increase in oxygen uptake rate (*OUR*) by the bacteria, which leads to an overall decrease in the required *SOTR* with increasing *SRT*.

If nitrification and denitrification as well as the reduction of the load by preliminary sedimentation is accounted for in the calculations, the same required *SOTR* is achieved for simultaneous aerobic sludge stabilization plants (*SRT* > 25 d) than for wastewater treatment plants with separate sludge stabilization and preliminary sedimentation. This result explains the similar energy demands observed during operation for both plant designs, although the simultaneous aerobic sludge stabilization plants convert a 30 % higher organic load and have better effluent quality. However, this result does not include the additional energy production of anaerobic digestion. Whether the additional energy production in activated sludge plants with separate sludge stabilization compensates for the lower labor, machinery and construction costs of simultaneous aerobic stabilization plants has to be critically analyzed.

Comparing the operation options during the summer period reveals that reducing the *SRT* to the minimum required at a particular temperature by decreasing the sludge concentration (floc volume) does not lead to a significant saving in the required *SOTR*. A positive effect of lowering the sludge concentration may be observed only if a similar adsorption and degradation capacity at the minimum required *SRT* is assumed. However, the dependency of the α-factor on the temperature-dependent minimum *SRT* has yet to be studied. The currently available data indicate an increase in the α-factor up to an *SRT* of 30 d, although the calculated minimum required *SRT* for sludge stabilization has already been achieved.

7 Outlook

The application of a variable α-factor is, as yet, not applied in practice. The new method provides the opportunity to better approximate the α-factor than using a fixed α-factor for all applications. However, since it is a new method and some parameters necessary for an approximation like the floc volume have not been determined in the past, the database for comparison is still scarce. Consequently, one future challenge is to collect data from existing wastewater treatment plants in relation to *MLVSS* concentration, floc volume, temperature and sludge retention time. A relatively easy method to obtain a first approximation is to measure the energy consumption of the blowers separately and to compare the values with the rate of conversion of organics and ammonium in the aeration basin. Doing so, the effect of blower aging is already incorporated and a comparison of the different options for action mentioned in Section 5.5.2 might be verified.

From the scientific point of view, this study has raised several questions. We still do not know, at the microscopic level, why the floc volume influences fine and coarse bubble aeration systems in the same way. Another unresolved question is why high airflow rates result in lower α-factors. The use of iron hydroxide flocs (see above), which are much easiear to handle than activated sludge, may lead to a more detailed understanding of these phenomena.

Another important challenge is to study the change of floc characteristics at different *SRT* and temperature and its effect on the α-factor. Besides measuring the degradation rate and floc volume it should also include the investigation of adsorption phenomena. Solving this problem will lead to an optimized design and operation of activated sludge plants.

Final remarks

The α-factor should be used as a parameter that reflects the impact of the sludge characteristics on the oxygen transfer. However, sometimes it is impossible to reduce the results to this simple view. For example, in real wastewater plants, diffuser aging is difficult to prevent, and its effect on oxygen transfer may be positive and negative (Loock (2009)). Another example is the impact of liquid flow. In practice, clean water tests are often performed while the plant is not in operation. In contrast, the measurements during operation in many cases include recirculation and agitation. In this case, the quotient of wastewater and clean water $k_L a$ will not deliver the α-factor but some composite parameter, which incorporates the characteristics of the sludge and the hydrodynamics of the plant.

8 Zusammenfassung

Der Sauerstoffeintrag zur Deckung des von den Mikroorganismen benötigten Sauerstoffbedarfs im Belebungsverfahren trägt zu einem wesentlichen Anteil der Gesamtenergiekosten einer Kläranlage bei (~ 60 %). Trotz zahlreicher Untersuchungen bezüglich der Einflussfaktoren auf den Sauerstoffeintrag sind die unterschiedlichen Ergebnisse bisher nicht zusammengeführt und in einem einheitlichen Konzept dargestellt worden. Dies gilt besonders für den Einfluss des Schlammes auf den Stoffübergang und das Verhalten oberflächenaktiver Substanzen im Dreiphasengemisch Belebtschlamm.

Ziel dieser Arbeit ist es, die komplexen Wechselwirkungen zwischen Feststoff-, Flüssig- und Gasphase auf den Stoffübergang darzustellen und den Einfluss von Belebtschlamm zu ermitteln. Dies beinhaltet auch die Untersuchung der Wirkung oberflächenaktiver Substanzen im adaptierten Belebtschlammgemisch. Zur Beurteilung der Ergebnisse wird der α-Wert herangezogen, der den Quotienten aus Sauerstoffeintragskoeffizient im kontaminierten System (Belebtschlamm, Überstand etc.) zu dem im Reinwasser darstellt. Insgesamt werden drei Versuchsphasen durchgeführt:

a) Versuchsreihe 1 (Greywater Experiments Part I)
untersucht den Einfluss von grob- und feinblasigen Belüftungssystemen auf den α-Wert bei unterschiedlichen Feststoffkonzentrationen unter Verwendung künstlich hergestellten Grauwassers. Trotz des Einsatzes grundsätzlich verschiedener Reaktorkonfigurationen (Schlaufenreaktor, Blasensäule) sinkt der α-Wert unabhängig von dem eingesetzten Belüftungssystem mit steigendem Trockensubstanzgehalt (TS-Konzentration) in gleicher Weise. Ein Vergleich mit existierenden Datensätzen unter Verwendung der für gewöhnlich gewählten TS-Konzentration zeigt zunächst eine deutliche Streuung. Wird statt der TS-Konzentration der organische Trockensubstanzgehalt (oTS-Konzentration) als Vergleichsparameter herangezogen, verbessert sich die Korrelation erheblich.
Weiterhin zeigt sich, dass der Einfluss handelsüblicher Tenside (oberflächenaktiver Substanzen) auf den Stoffübergang in einem adaptierten System bei hohen Schlammaltern (> 25 d) trotz erhöhter Zulaufkonzentration (~ 70 mg/L) vernachlässigbar ist. In der flüssigen Phase (Ablauf Membrananlage) konnte kein Einfluss auf den Stoffübergangskoeffizienten gemessen werden (α-Wert = 1).
Aus den Ergebnissen der Versuchsreihe 1 wurde die Arbeitshypothese abgeleitet, dass weniger die Viskosität oder oberflächenaktive Substanzen für dieses Verhalten verantwortlich sind, sondern vielmehr der freie Wasseranteil respektive das Flockenvolumen der Suspension.

b) In Versuchsreihe 2 (Greywater Experiments Part II)
wird mittels einer eigens entwickelten Methode (Hydrostatisches Flockenvolumen, HFV) der Einfluss des Flockenvolumens unter Verwendung von Eisenhydroxidflocken verdeutlicht. Mit zunehmendem Flockenvolumen respektive abnehmendem freien Wasseranteil sinkt der α-Wert unter Verwendung eines feinblasigen Belüftungssystems bis zu einem Flockenvolumen von 500 mL/L linear ab. Biologische Prozesse können demnach als Ursache für dieses Phänomen ausgeschlossen werden.

Weiterhin wird durch gezielte Veränderung des Schlammalters der unterschiedliche Einfluss der oTS- im Vergleich zur TS-Konzentration herausgearbeitet. Die Ergebnisse verdeutlichen, dass zum einen der Feststoffgehalt im Zulauf als auch das Abbau-/Adsorptionsverhalten bzw. Biomassewachstum bei unterschiedlichen Schlammaltern als ein Grund für die große Streuung der bisher beobachteten α-Werte genannt werden kann. Wie schon in der ersten Versuchsreihe wird eine bessere Korrelation des α-Werts unter Verwendung der oTS-Konzentration erreicht.
Trotz geringerem Schlammalter (~ 12 d) und erhöhter Tensidkonzentration im Zulauf (~ 60 mg/L) kann kein Einfluss auf den Sauerstoffübergangskoeffizienten in der flüssigen Phase (Ablauf Membrananlage) festgestellt werden. Vielmehr deutet sich an, dass an der Schlammflocke adsorbierte, schwerer abbaubare Substanzen (langkettige Fettsäuren) mit der Luftblase wechselwirken und so zu einem tendenziell niedrigeren α-Wert führen, als dies allein durch das Flockenvolumen zu erwarten wäre.

c) Versuchsreihe 3 (Wastewater Experiments)
widmet sich Versuchen mit realem Abwasser und dessen Einfluss auf den α-Wert. Ein Vergleich der α-Werte mit denen der Grauwasserexperimente ergibt erneut eine bessere Übereinstimmung, wenn die oTS- statt der TS-Konzentration als Vergleichsparameter herangezogen wird.
Versuche mit 24 h belüfteten Schlamm und Eisenhydroxidflocken bei unterschiedlichen Feststoffkonzentrationen mit grob- und feinblasigen Belüftungssystemen unter Verwendung des hydrostatischen Flockenvolumens als Referenzparameter zeigen eine starke Übereinstimmung. Damit wird der Einfluss des Flockenvolumens auf den α-Wert verdeutlicht. Folglich lassen sich die Ergebnisse aus der ersten Versuchsreihe mit Grauwasserschlamm auf den Effekt des Flockenvolumens zurückführen, der grob- und feinblasige Belüftungssysteme in gleicher Weise negativ beeinflusst.
Weiterhin kann gezeigt werden, dass ein Großteil der oberflächenaktiven Substanzen bereits im Zulauf gebunden an der Feststoffphase vorliegt. Versuche unter Zugabe von Pulveraktivkohle zu Reinwasser, Abwasser und Belebtschlamm sowie mit Membrananlagen in Betrieb bestärken die Hypothese einer Wechselwirkung zwischen den an der Feststoffphase gebundenen oberflächenaktiven Substanzen und der hydrophoben Oberfläche der Luftblase.
Bezüglich des Einflusses von in der flüssigen Schlammphase gelösten oberflächenaktiven Substanzen (Ablauf Membrananlage), kann gezeigt werden, dass deren Einfluss auf den α-Wert gering ist. Erst bei einem Schlammalter kleiner 8 d (in diesem Fall 2 d) konnte ein negativer Effekt beobachtet werden.
Generell stellt sich heraus, dass speziell bei erhöhtem Feststoffgehalt mit steigender Luftbeaufschlagung zwar der Sauerstoffübergangskoeffizient steigt, der α-Wert allerdings sinkt und damit zu einer Verschlechterung der Sauerstoffeintragseffizienz führt.
Ein weiteres Indiz dafür, dass das Flockenvolumen besser durch die oTS- als durch die TS-Konzentration abgebildet werden kann, liefert der Vergleich des Vergleichsschlammvolumens (VSV) der Grauwasser- und der Abwasserexperimente. Während die Korrelation mit der TS-Konzentration keine Übereinstimmung der Ergebnisse ergibt,

zeigt sich bei Verwendung der oTS-Konzentration eine sehr gute Übereinstimmung. Damit lässt sich unterschiedliches Sedimentationsverhalten bei Abwesenheit von Blähschlamm rein auf sterische Effekte (behindertes Absetzen) zurückführen. Die Ergebnisse verdeutlichen, dass die TS-Konzentration ein ungeeigneter Parameter für die Beschreibung von Phänomenen ist, bei denen das Flockenvolumen eine entscheidende Rolle spielt (Sauerstoffeintrag, Sedimentationsverhalten).

Mit der Kenntnis des prinzipiell unterschiedlichen Einflusses von Flockenvolumen und Schlammalter auf den α-Wert wird im Anschluss an die Versuchsreihen ein übergreifender Zusammenhang hergestellt. Demnach sinkt bei gleichbleibendem Schlammalter mit steigendem Flockenvolumen der α-Wert linear bis zu einem Flockenvolumen von ca. 500 mL/L (~ 12 g/L oTS). Bei konstantem Flockenvolumen steigt hingegen der α-Wert mit zunehmenden Schlammalter bis ca. 30 d linear an. Mit Hilfe eigener sowie fremder Daten lässt sich dieser Zusammenhang mathematisch wie folgt formulieren:

$$\alpha - Wert = 0{,}51 - 0{,}062 \cdot oTS + 0{,}019 \cdot t_{TS} \qquad \pm 0{,}114$$

mit

oTS	[g/L]	organischer Trockensubstanzgehalt [1 - 12 g/L]
t_{TS}	[d]	Schlammalter [1 - 30 d]

Aufgrund der hohen Schwankungsbreite der Basisdaten insbesondere der Beziehung zwischen Schlammalter und α-Wert lassen sich hiermit noch keine exakten Werte vorausbestimmen. Dies ist auch dadurch begründet, dass eine Vorhersage der sich später in der Praxis einstellenden oTS-Konzentration schwierig ist.

Allerdings ermöglicht diese Formel einen Vergleich der Ermittlung der erforderlichen Sauerstoffzufuhr mit der bisher üblichen Vorgehensweise einer konstanten α-Wert Wahl. Es zeigt sich, dass mit der neuen Berechnung bei konstanter oTS-Konzentration der ansteigende Sauerstoffbedarf der Bakterien für die Oxidation organischer Substanzen mit steigendem Schlammalter durch den Anstieg des α-Wertes überkompensiert und die erforderliche Sauerstoffzufuhr reduziert wird, während diese nach der bisherigen Methode stetig steigt. Werden bei der Berechnung auch Nitrifikation und Denitrifikation sowie die Verminderung der Zulauffracht zur Belebung durch die Vorklärung berücksichtig, ergibt sich die gleiche erforderliche Sauerstoffzufuhr für aerobe Stabilisierungsanlagen im Vergleich zu Kläranlagen mit separater Schlammstabilisierung und Vorklärung. Dieses Ergebnis erklärt auch den in der Praxis beobachteten, bisher ungeklärten gleichen Energieverbrauch aerob stabilisierender Anlagen im Vergleich zu letzteren, obwohl erstere eine wesentlich höhere Fracht verarbeiten, bei gleichzeitig besseren Ablaufwerten. Allerdings wird bei diesem Vergleich nicht die zusätzliche Energieerzeugung einer anaeroben Schlammstabilisierung betrachtet. Ab welcher Größenklasse diese Energieerzeugung sich mit den niedrigeren Personal-, Maschinen- und Baukosten aerob stabilisierender Anlagen gegenrechnet, gilt es kritisch zu prüfen.

Eine weiterer Vergleich verschiedener Handlungsoptionen für den Betrieb von Kläranlagen im Sommer kommt zu dem Ergebnis, dass bezüglich der benötigten Sauerstoffzufuhr ein Konstanthalten der TS-Konzentration sich nicht wesentlich von der Option des Anpassens an

das im Sommer niedrigere Mindestschlammalter durch Absenken der TS-Konzentration unterscheidet. Lediglich unter der Annahme, dass das Adsorptions- und Abbauverhalten bei den jeweiligen Mindestschlammaltern gleich wäre, ließe sich ein positiver Effekt durch Absenken der TS-Konzentration bei niedrigerem Schlammalter erzielen, wobei die Abhängigkeit des α-Wertes bezüglich des temperaturabhängigen Mindestschlammalters bisher nicht untersucht wurde. Die vorhandenen Untersuchungen weisen darauf hin, dass der α-Wert bei konstantem Flockenvolumen weiterhin bis zu einem Schlammalter von 30 d anzusteigen scheint, obwohl theoretisch bereits eine Schlammstabilisierung erreicht wurde.

Ausblick

Eine variable Anpassung des α-Wertes an das gewählte Schlammalter und Flockenvolumen ermöglicht eine bessere Abschätzung der tatsächlich benötigten Sauerstoffzufuhr im Belebtschlammverfahren. Allerdings ist die Datenbasis noch spärlich. Von daher wird eine zukünftige Aufgabe darin bestehen, weitere Daten von real existierenden Anlagen unter Berücksichtigung der Parameter wie oTS-Konzentration, Flockenvolumen, Temperatur und Schlammalter zu sammeln und diese mit den bereits gewonnen Daten zu vergleichen.

Eine erste Abschätzung, welche der vorgestellten Handlungsoptionen in der Praxis tatsächlich zu einem niedrigeren Energieverbrauch führt, könnte durch getrennte Erfassung des Energieverbrauches der Gebläse vorgenommen werden. Durch die parallele Erfassung der dem Belebungsbecken zufließenden Frachten (CSB, BSB, NH_4) sollte sich die Auswirkung eines niedrigeren Schlammalters durch Absenkung der TS-Konzentration zuordnen lassen.

Aus Sicht der Grundlagenforschung bleibt weiterhin zu klären, welcher mikroskopische Effekt dazu führt, dass das Flockenvolumen feinblasige als auch grobblasige Belüftungssysteme in gleicher Weise beeinflusst. Dies gilt auch für die Auswirkung eines erhöhten Luftvolumenstromes auf den α-Wert speziell bei erhöhtem Flockenvolumen und Stoffübergangskoeffizienten.

Wichtig für die zukünftige Auslegung von Kläranlagen ist die differenziertere Betrachtung der Abhängigkeit des α-Wertes vom Schlammalter bei unterschiedlichen Temperaturen unter Berücksichtigung des Flockenvolumens und des Adsorptionsverhaltens des Schlammes.

Anmerkung

Der α-Wert sollte als Parameter gebraucht werden, welcher den Einfluss der Schlammeigenschaften auf den Sauerstoffeintrag widerspiegelt. Diese „einfache“ Anforderung kann in der Praxis nur schwierig erfüllt werden. Die zeitlich bedingte Differenz zwischen Reinwasser- und Betriebsmessung beinhaltet Veränderungen der Belüfter an sich, die sich sowohl positiv als auch negativ auf den Stoffübergang auswirken können (Loock (2009)). Weiterhin herrschen während des Betriebs oft andere hydrodynamische Bedingungen als während der Reinwassermessung. Der unter diesen Umständen bestimmte α-Wert schließt folglich all diese Effekte mit ein und reflektiert somit nicht nur die Eigenschaften des Schlammes.

9 Epilog

The tension between knowledge and ignorance leads to problems and to tentative solutions. Yet the tension is never overcome. For it turns out that our knowledge only ever consists in suggestions for provisional and tentative solutions. Thus the very idea of knowledge involves, in principle, the possibility that it will turn out to have been a mistake, and therefore a case of ignorance. And the only way of justifying our knowledge is itself merely provisional, for it consists in criticism or, more precisely, in an appeal to the fact that so far our attempted solutions appear to withstand even our most penetrating criticism.

Die Spannung zwischen Wissen und Nichtwissen führt zum Problem und zu den Lösungsversuchen. Aber sie wird niemals überwunden. Denn es stellt sich heraus, dass unser Wissen immer nur in vorläufigen und versuchsweisen Lösungsvorschlägen besteht und daher prinzipiell die Möglichkeit einschließt, dass es sich als irrtümlich und als Nichtwissen herausstellen wird.

Die einzige Form der Rechtfertigung unseres Wissens ist wieder nur vorläufig: Sie besteht in der Kritik, oder genauer darin, dass unsere Lösungsversuche bisher auch unserer scharfsinnigsten Kritik standzuhalten scheinen.

Karl Popper 1962: Die Logik der Sozialwissenschaften, in: Theodor W. Adorno u.a.: Der Positivismusstreit in der deutschen Soziologie, Darmstadt, S. 103

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11 Appendix

11.1 Daily required standard oxygen transfer rate

The daily required standard oxygen transfer rate (*SOTR,* [kg O_2/d]) can be calculated with the following formula (Mueller et al. (2002)):

$$SOTR = OTR_{field} \cdot \left(\frac{c_{S,20}}{(\beta \cdot \Omega \cdot c_{S,T} - c) \cdot \theta^{T-20} \cdot \alpha} \right) \qquad (11\text{-}1)$$

with

OTR_{field}	[kg O_2/d]	Oxygen transfer rate required under process conditions
$c_{S,20}$	[mg/L]	Oxygen saturation concentration at 20 °C
c	[mg/L]	Oxygen concentration under process conditions
$c_{S,T}$	[mg/L]	Oxygen saturation concentration under process conditions
β, Ω	[-]	Salt, pressure correction factor for oxygen concentration
θ	[-]	Temperature correction factor for oxygen transfer coefficient
α	[-]	α-factor

The OTR_{field} equals the total amount of oxygen required for the oxidation of organic compounds (OUR_{BOD}) and the nitrification of ammonium (OUR_{NH4}). Denitrification reduces the organic load to the aeration tank and therefore must be considered in the overall calculation (oxygen saving rate, OSR_{NO3}). According to the German Standard ATV 131 (ATV-DVWK (2000)) the single oxygen uptake/saving rate can be calculated as follows:

a) $$OUR_{BOD} = L_{BOD,inf\ luent} \cdot \left(0.56 + \frac{0.15 \cdot SRT \cdot 1.072^{T-15}}{1 + 0.17 \cdot SRT \cdot 1.072^{T-15}} \right) \qquad (11\text{-}2)$$

with

OUR	[kg O_2/d]	Oxygen uptake rate by the microorganisms
$L_{BOD,influent}$	[kg/d]	Influent *BOD* load to the aeration tank
SRT	[d]	Sludge retention time
T	[°C]	Temperature

b) $$OUR_{NH_4} = L_{NH_4,oxidized} \cdot 4.3 \qquad (11\text{-}3)$$

with

$L_{NH4,oxidized}$	[kg/d]	Oxidized ammonia load

c) $$OSR_{NO_3} = L_{NO_3,removed} \cdot 2.9 \qquad (11\text{-}4)$$

with

$L_{NO3,removed}$	[kg/d]	Removed nitrate load in the denitrification zone

The OTR_{field} can then be calculated as follows:

$$OTR_{field} = OUR_{BOD} + OUR_{NH_4} - OSR_{NO_3} \qquad (11\text{-}5)$$

11.2 Exemplary calculation of the required standard oxygen transfer rate (SOTR) for different plant designs: data base

For the calculations of the required *SOTR* the following inhabitant-specific loads were assumed:

Table 14: Inhabitant-specific loads according to German Standard ATV 131 (ATV-DVWK (2000))

		Raw wastewater	After preliminary sedimentation (1.5 - 2 h)
COD load	g/(C·d)	120	80
BOD_5 load	g/(C·d)	60	40
TKN load	g/(C·d)	11	10
SS load	g/(C·d)	70	25

Further assumptions:

- Inhabitant-specific flow = 120 L/(C·d)
- The required *SOTR* refers to the daily load and does not include peak loads or safety factors
- The Total Kjeldahl Nitrogen load (TKN load) entering the plant is present as ammonium (NH_4-N).
- All ammonium is completely oxidized to nitrate (NO_3-N)
- The plants which include denitrification denitrify 80 % of the nitrate.
- Neither ammonium nor nitrate is incorporated by the bacteria
- All the BOD_5 load is degraded
- No salt nor height correction is applied to the *SOTR* calculation
- The loss on ignition is 80 %
- The oxygen concentration under process conditions is 2 mg/L
- The *SRT* incorporates the nitrification and denitrification reactor volume
- The temperature for all calculations is 12°C, except for the seasonal adaption calculations where 20°C are assumed

11.3 Forces acting at the bubble

Figure 52 shows a sketch of the forces acting at the bubble. The force balance according to Bals (2002) and Yang et al. (2007) can be expressed as follows:

$$F_\sigma + F_D = (F_B - F_W) + F_{IL} + F_{IG} + F_F + F_{dB} + F_M \qquad (11\text{-}6)$$

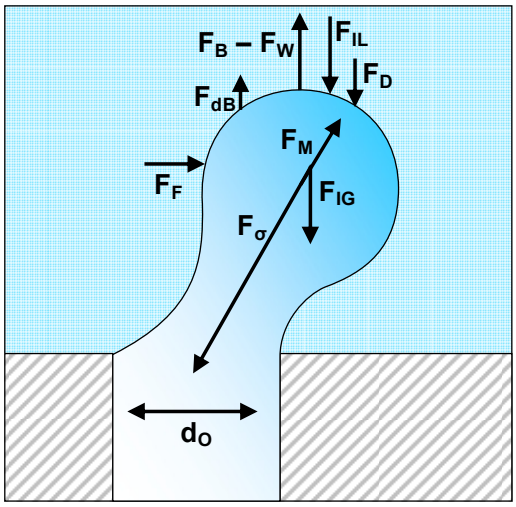

Figure 52: Force balance at the bubble surface (adapted from Bals (2002))

where

a) The Surface Tension Force $F\sigma$ at the orifice is calculated by the orifice diameter d_O [m] and the surface tension σ [N/m]

b) $(F_B - F_W)$ describes the Effective Buoyancy Forces, the difference between the Buoyant Force F_B and the Weight Force F_W, resulting from the density differences of the two phases $(\rho_L - \rho_G)$ [kg/m³], the gravitational acceleration g [m/s^2] and the replaced liquid volume which is equal to the bubble volume V_B [m³]

c) The Drag Force F_D depends on the drag coefficient c_d [-], the relative bubble rise velocity of the bubble $w_{B,rel}$ [m/s], the density of the liquid ρ_L [kg/m³] and the bubble diameter d_B [m]

d) The Fluid Flow Force F_F gets important when the fluid is in motion, with w_L [m/s] describing the liquid flow velocity

e) F_{dB} is named the Dynamic Buoyant Forces, induced by the Fluid Flow Force, where τ_W [Pa] is the shear stress and η [Pa·s] the apparent dynamic viscosity

f) The Liquid Inertial Force F_{IL} describes the force which is induced through the acceleration of the liquid surrounding the bubble during expansion

g) The Gas Inertial Force F_{IG} and the Gas Momentum Force F_M get relevant at high gas volume streams, where the surface tension forces loosen their influence

Table 15: Expression of the forces involved in the bubble formation process

Forces	Calculation	Units	
Surface Tension Force	$F_\sigma = d_O \cdot \pi \cdot \sigma(t)$	$\left[m \cdot \frac{N}{m} \right]$	(11-7)
Effective Buoyancy Forces	$F_{B-W} = (\rho_L - \rho_G) \cdot g \cdot V_B$	$\left[\frac{kg}{m^3} \cdot \frac{m}{s^2} \cdot m^3 \right]$	(11-8)
Drag Force	$F_D = c_d \cdot \frac{w_{B,rel}^2 \cdot \rho_L}{2} \cdot \frac{d_B^2 \cdot \pi}{4}$	$\left[\frac{m^2}{s^2} \cdot \frac{kg}{m^3} \cdot m^2 \right]$	(11-9)
Fluid Flow Force	$F_F = c_d \cdot \frac{w_L^2 \cdot \rho_L}{2} \cdot \frac{d_B^2 \cdot \pi}{4}$	$\left[\frac{m^2}{s^2} \cdot \frac{kg}{m^3} \cdot m^2 \right]$	(11-10)
Dynamic Buoyant Force	$F_{dB} = 0.76 \frac{\tau_W^{1.5} \cdot d_B^3 \cdot \rho_L^{0.5}}{\eta_L}$	$\left[\left(Pa^3 \cdot m^6 \cdot \frac{kg}{m^3} \cdot \frac{1}{Pa^2 \cdot s^2} \right)^{0.5} \right]$	(11-11)
Liquid Inertial Force	$F_{IL} = \frac{\delta(\rho_L \cdot V_B \cdot w_{B,rel})}{\delta t}$	$\left[\frac{kg}{m^3} \cdot m^3 \cdot \frac{m}{s^2} \right]$	(11-12)
Gas Inertial Force	$F_{IG} = \frac{\delta(\rho_G \cdot V_B \cdot w_{B,rel})}{\delta t}$	$\left[\frac{kg}{m^3} \cdot m^3 \cdot \frac{m}{s^2} \right]$	(11-13)
Gas Momentum Force	$F_M = \frac{4}{\pi \cdot d_O^2} \cdot Q^2 \cdot \rho_G$	$\left[\frac{1}{m^2} \cdot \frac{m^6}{s^2} \cdot \frac{kg}{m^3} \right]$	(11-14)

11.4 The formation of bubbles according to Kumar and Kuloor

According to Kumar and Kuloor (1970) the "Force Balance Bubble Volume" (V_{fb}) can be expressed as follows:

$$V_{fb}^{5/3} = \frac{11 \cdot Q^2}{192 \cdot \pi \cdot \left(\frac{3}{4 \cdot \pi}\right)^{2/3} \cdot g} + \frac{3 \cdot \eta_L \cdot Q}{2 \cdot \left(\frac{3}{4 \cdot \pi}\right)^{1/3} \cdot g \cdot \rho_L} \cdot V_{fb}^{1/3} + \frac{\pi \cdot d_O \cdot \sigma \cdot \cos\varphi}{g \cdot \rho_L} \cdot V_{fb}^{2/3} \quad (11\text{-}15)$$

where

V_{fb}	[m³]	[cm³]	Force balance bubble volume
Q	[m³/h]	[cm³/s]	Volumetric flow rate
g	[m/s²]	[cm/s²]	Gravitational acceleration
η_L	[Pa s]	[poise]	Dynamic viscosity of the liquid
ρ_L	[kg/m³]	[gm/cm³]	Liquid density
d_O	[m]	[cm]	Orifice diameter
σ	[N/m]	[dyn/cm]	Surface tension
φ	[degrees]	[degrees]	Contact angle

The first row of units equals to the SI standard, while the second row represent the units used in the calculations of Kumar and Kuloor.

The equation can be used in any situation when the bubble formation is taking place under constant flow conditions. The first term expresses the bubble formation without considering surface tension and viscosity effects. The second term introduces the viscosity effect while the third term introduces the surface tension effect.

To determine the final the bubble volume (V_F) which includes the expansion of the bubble Kumar and Kuloor propose the following equation:

$$r_{fb} = \frac{B}{2 \cdot Q \cdot (A+1)} \cdot \left(V_F^2 - V_{fb}^2\right) - \frac{E}{A \cdot Q} \cdot \left(V_F - V_{fb}\right) - \frac{3 \cdot C}{2 \cdot Q \cdot (A - 1/3)} \cdot \left(V_F^{2/3} - V_{fb}^{2/3}\right) \quad (11\text{-}16)$$

where

$$A = 1 + \frac{1.25 \cdot 6 \cdot \pi \cdot \left(\frac{3}{4 \cdot \pi}\right)^{1/3} \cdot \eta_L}{Q \cdot \left[\rho_G + \left(\frac{11}{16}\right) \cdot \rho_L\right]} \cdot V_{fb}^{1/3} \quad (11\text{-}17)$$

$$B = \frac{(\rho_L - \rho_G) \cdot g}{Q \cdot \left[\rho_G + \left(\frac{11}{16}\right) \cdot \rho_L\right]} \quad (11\text{-}18)$$

$$C = \frac{3 \cdot \eta_L}{2 \cdot \left(\frac{3}{4 \cdot \pi}\right)^{1/3} \cdot \left[\rho_G + \left(\frac{11}{16}\right) \cdot \rho_L\right]} \quad (11\text{-}19)$$

$$E = \frac{\pi \cdot d_O \cdot \sigma \cdot \cos\varphi}{Q \cdot \left[\rho_G + \left(\frac{11}{16} \right) \cdot \rho_L \right]} \qquad (11\text{-}20)$$

ρ_G	[kg/m³]	[gm/cm³]	Gas density
r_{fb}	[m]	[cm]	Radius of the force-balance bubble

Knowing V_{fb} and the other system characteristics, the final bubble volume V_F can be directly calculated from Equation 11-16.

		coarse bubble	fine bubble
Slit flow rate	cm³/s	138	0.09
Orifice diameter	mm	5	0.25
Gravitational acceleration	cm/s²	981	981
Liquid density	gm/cm³	1.00	1.00
Gas density	gm/cm³	0.0013	0.0013
Surface tension	dyn/cm	72	72
Liquid viscosity	poise	0.0001	0.0001
Final bubble volume	cm³	4.39	0.0075
Bubble diameter (circular)	mm	20.3	2.4
Dominant Force		Liquid inertia (F_{IL})	Surface tension (F_σ)

11.5 Impact of viscosity on α-factor for fine and coarse bubbles

Although viscosity has no effect on bubble formation and bubble rise behavior in the usual scope of activated sludge processes, it may influence the diffusion of oxygen into the media. According to the Einstein–Smoluchowski relation, the diffusion coefficient (D, [m²/s]) is expressed as:

$$D = \frac{k_B \cdot T}{3 \cdot \pi \cdot r_{O_2} \cdot \eta_L} \qquad (11\text{-}21)$$

with

k_B	[kg·m²/(s²·K)]	Boltzmann's constant
T	[K]	Temperature
r_{O_2}	[m]	Diameter of oxygen molecule
η_L	[Pa s]	Dynamic viscosity of the liquid

With this equation and the transformation of Higbie (see Section 3.2.1), k_La for a single bubble can be expressed as:

$$k_L a = 2\sqrt{\left(\frac{k_B \cdot T}{3 \cdot \pi \cdot r_{O_2} \cdot \eta_L} \cdot \frac{w_B}{\pi \cdot d_B}\right)} \cdot a \qquad (11\text{-}22)$$

As quoted before, bubble formation, and consequently bubble size as well, in fine and coarse bubble aeration is only influenced at very high viscosities (Gerlach et al. (2007)). Consequently, the bubble diameter can be assumed to be constant. Thus the α-factor which is defined as the quotient of oxygen transfer coefficient in the liquid studied (here viscous media, $k_La_{viscous}$) divided by the oxygen transfer coefficient in clean water (k_La_{clean}) turns into:

$$\alpha - factor = \frac{k_L a_{viscous}}{k_L a_{clean}} = \sqrt{\left(\frac{w_{B,viscous} \cdot \eta_{L,clean}}{\eta_{L,viscous} \cdot w_{B,clean}}\right)} \cdot \frac{a_{viscous}}{a_{clean}} \qquad (11\text{-}23)$$

In the following experiment, two reactors are equipped with a single orifice each, one with a diameter size of 0.025 mm and the other with a diameter of 0.5 mm. The first reactor produces fine bubbles (~ 2 mm) with a frequency of 16 1/s at an airflow rate of 0.1 cm³/s, according to the calculation of Kumar and Kuloor (1970) (see previous chapter). The second reactor produces coarse bubbles (~ 20 mm) with a frequency of 32 1/s at an airflow rate of 140 cm³/s. The lower rise velocity for fine bubble aeration at different viscosities (Figure 3) leads to a higher residence time of the bubbles and an increase in the superficial area a with increasing viscosity. In contrast, the rise velocity in the reactor with coarse bubble aeration is not affected by the viscosity and consequently the superficial area a stays constant. It turns out that under the above-mentioned assumptions the α-factor for fine bubble aeration systems should be higher than for coarse bubble aeration systems. According to this derivation, the biggest influence on the α-factor can be observed at low viscosities (<0.05 Pa·s). For coarse bubble aeration systems, the effect is only based upon the lower diffusion coefficient.

Table 16: Input data derived from the calculations according to Kumar and Kuloor (1970)

Input data		Fine bubble	Coarse bubble
Orifice diameter	mm	0.25	5
Bubble volume	mm³	7.5	4,390
Bubble diameter	mm	2.4	20.3
Flow rate	cm³/(slit·s)	0.09	138
Formation frequency	1/s	12,4	32
Bubble surface	mm²	19.6	1,294

Table 17: Calculations for fine bubbles

Viscosity Pa s	Rise velocity m/s	Residence time s	Number of bubbles	Surface aerea *a* mm²	α-factor
0.001	0.24	4.17	52	934	1.00
0.003	0.215	4.65	58	1,043	0.61
0.005	0.19	5.26	65	1,180	0.50
…	…	…	…	…	…

Table 18: Calculations for coarse bubbles

Viscosity Pa s	Rise velocity m/s	Residence time s	Number of bubbles	Surface aerea *a* mm²	α-factor
0.001	0.33	4	128	165,627	1.00
0.003	0.33	4	128	165,627	0.58
0.005	0.33	4	128	165,627	0.45
…	…	…	…	…	…

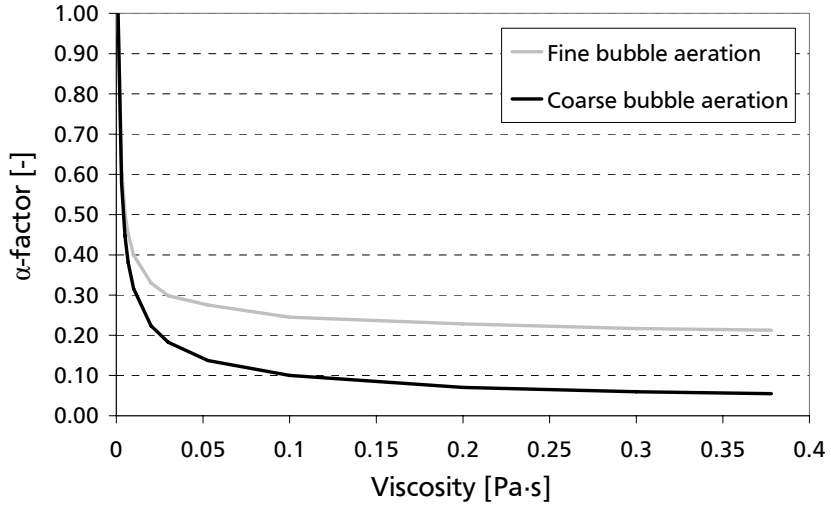

Figure 53: α-factor at different viscosities for fine and coarse bubbles

11.6 Weissenborn and Pugh (1996): Surface Tension of Aqueous Solutions of Electrolytes

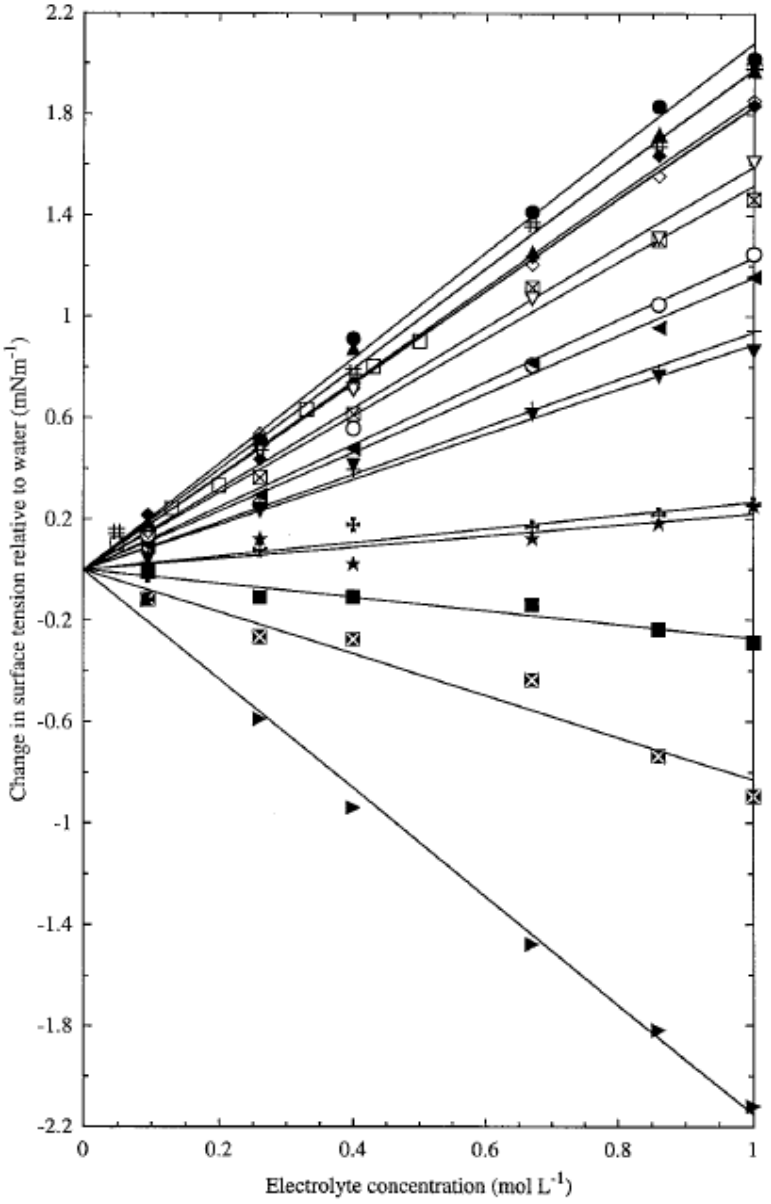

FIG. 3. Effect of electrolyte concentration on the change in surface tension relative to water for 1:1 electrolytes. Bubble interval, 1.5 s. Experimental error in data points is ±0.1 mN m^{-1}. HCl (■), LiCl (▲), NaCl (●), KCl (♦), CsCl (⊠), NaF (□), NaI (○), NH_4Cl (▽), NaBr (◇), HNO_3 (⊠), $(CH_3)_4NCl$ (+), NH_4NO_3 (◀), $HClO_4$ (▶), $NaClO_3$ (▼), $LiClO_4$ (✠), $NaClO_4$ (★), KOH (#).

Figure 54: Effect of electrolyte concentration on the change in surface tension

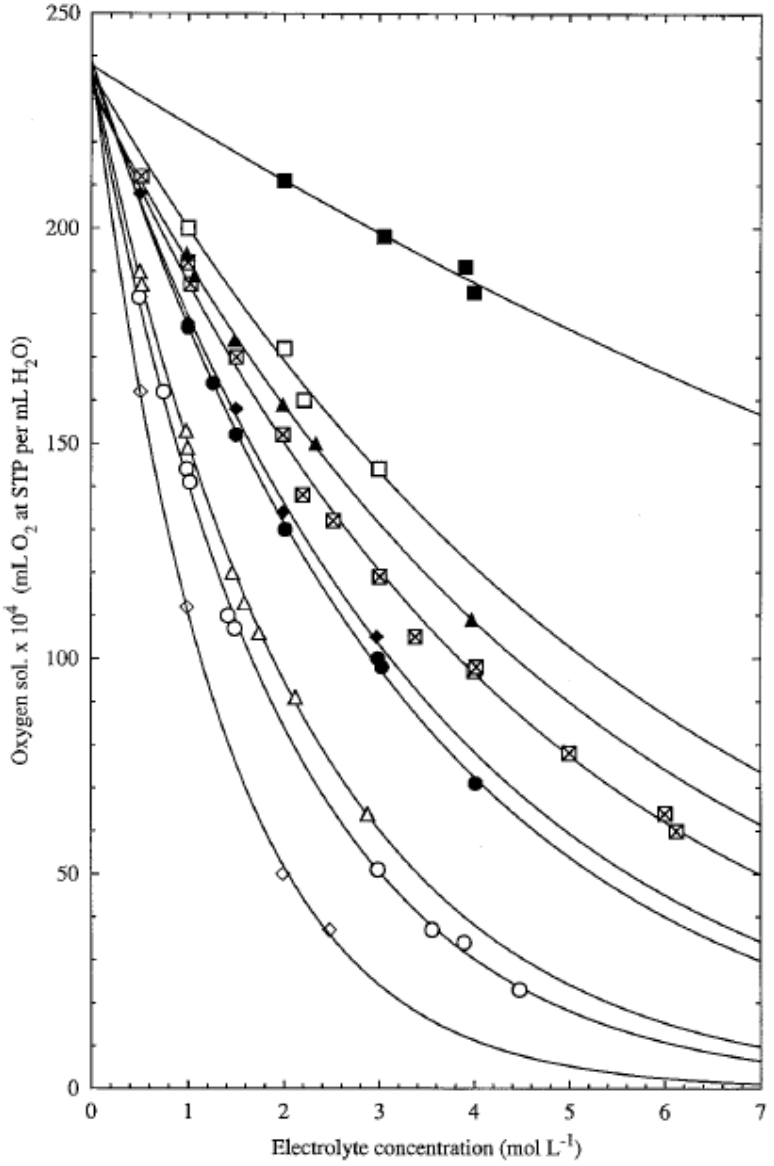

FIG. 10. Effect of electrolyte concentration (as chloride solutions) on the solubility of oxygen in water (Bunsen coefficients) at 37°C. Solubility of oxygen in pure water is 0.0240 mL O_2 at STP per mL H_2O. Solubility data taken from ref. (13). Exponential curve fit with decay coefficients given in brackets: HCl (■) (−0.06), LiCl (▲) (−0.19), NaCl (●) (−0.30), KCl (◆) (−0.28), CsCl (⊠) (−0.22), NH_4Cl (□) (−0.17), $MgCl_2$ (△) (−0.46), $CaCl_2$ (○) (−0.51), $LaCl_3$ (◇) (−0.76).

Figure 55: Effect of electrolyte concentration on the solubility of oxygen in water

11.7 Sardeing et al. (2006): Effect of surfactants on liquid-side mass transfer coefficients in gas–liquid systems

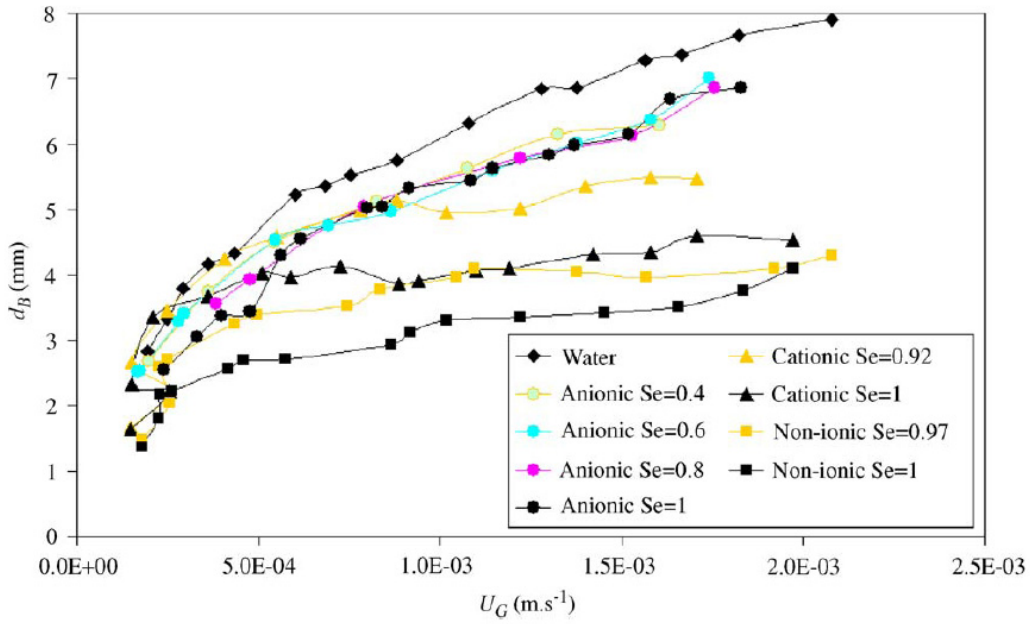

Figure 56: Effect of surfactants on bubble diameter at different *SGV*

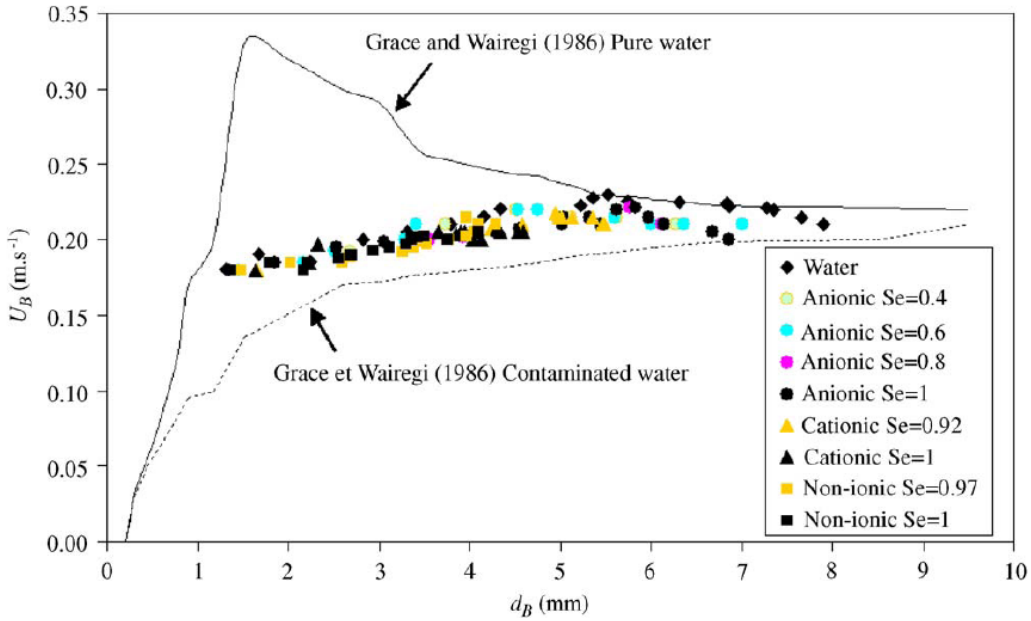

Figure 57: Effect of surfactants on terminal rising bubble velocity at different *SGV*

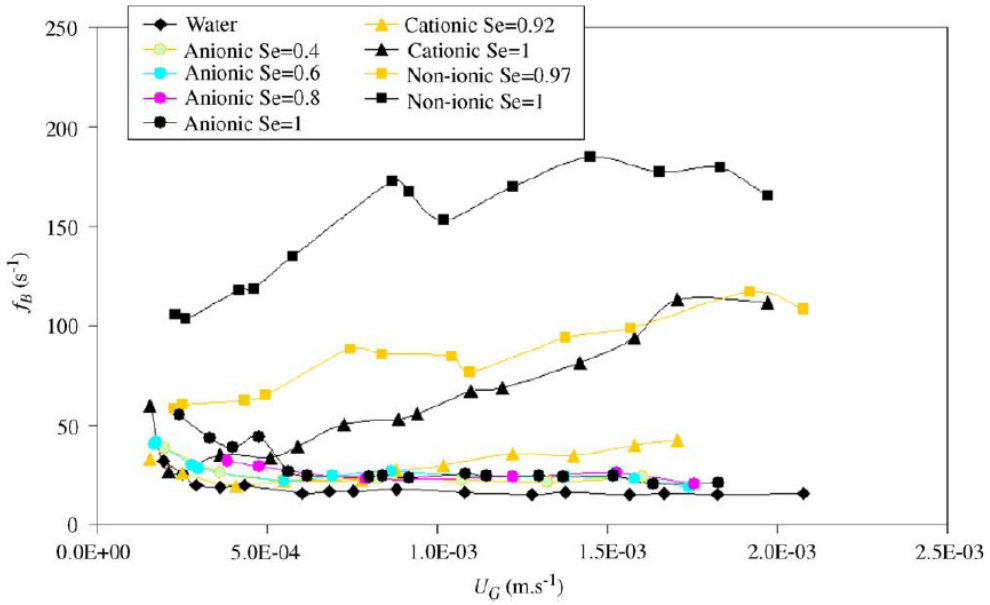

Figure 58: Effect of surfactants on bubble formation frequency at different *SGV*

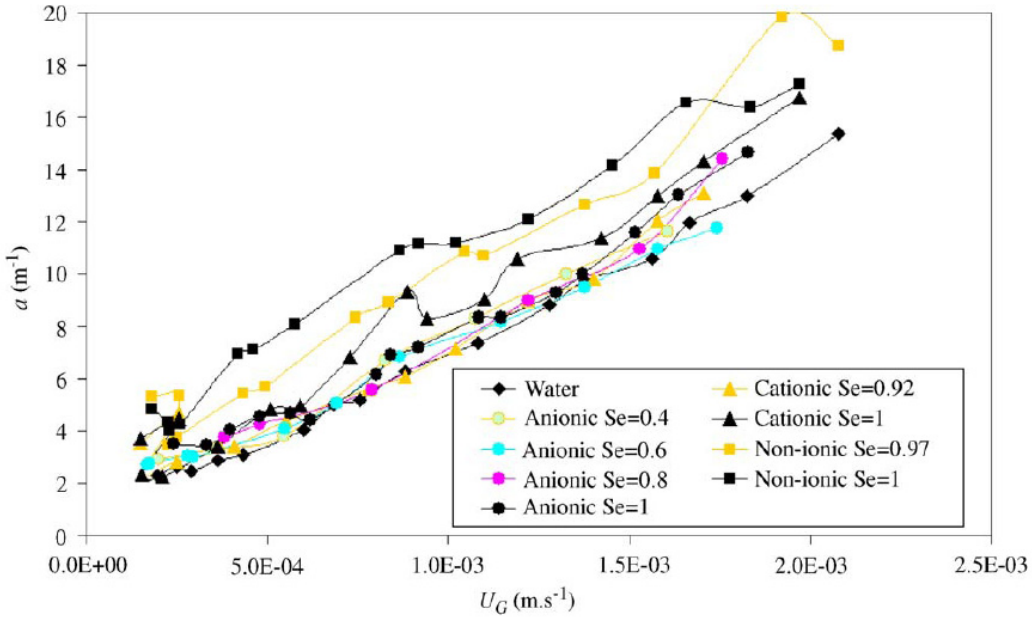

Figure 59: Effect of surfactants on specific interfacial area at different *SGV*

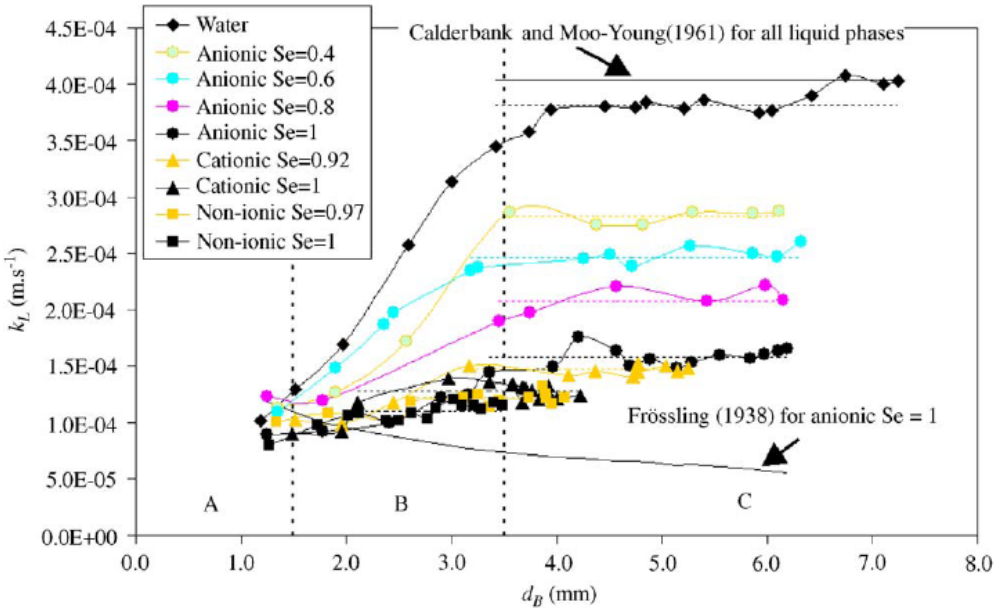

Figure 60: Effect of surfactants on liquid-side mass transfer coefficient at different bubble diameters

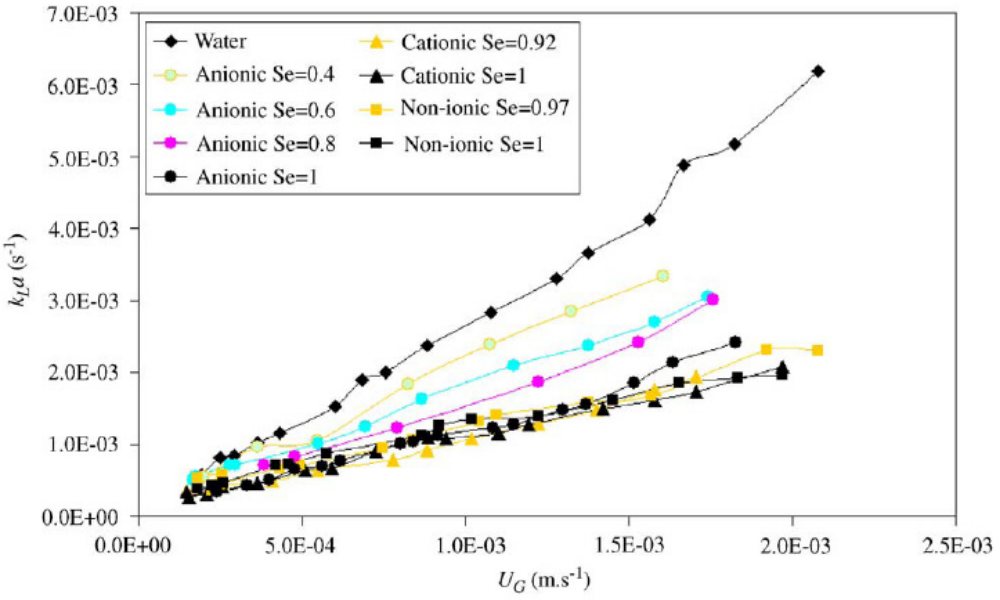

Figure 61: Effect of surfactants on volumetric mass transfer coefficient at different *SGV*

11.8 EPA (1989): Fine pore aeration systems

Figure 2-15. Effect of unit airflow rate on SOTE for fine pore tube diffusers.

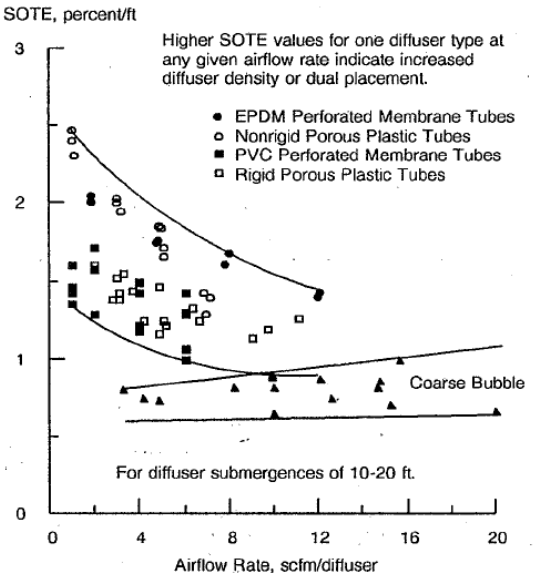

Figure 2-16. Effect of unit airflow rate on SOTE for ceramic dome/disc diffusers.

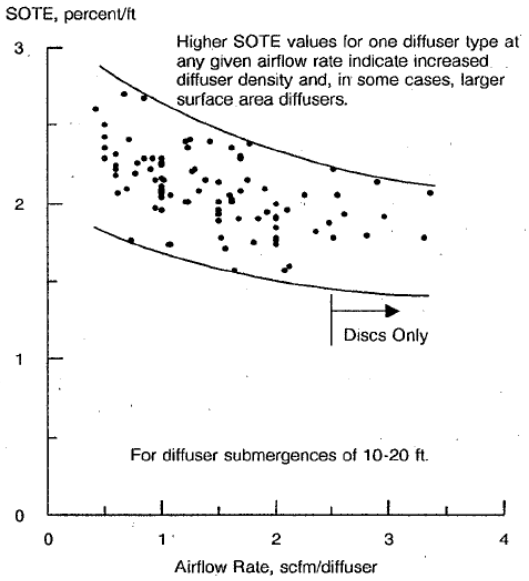

Figure 62: Correlation of specific oxygen transfer efficiency and airflow rate for coarse and fine bubble aeration systems

11.9 Sun and Furusaki (1989): Effect of intraparticle diffusion on the determination of the gas liquid volumetric oxygen-transfer coefficient

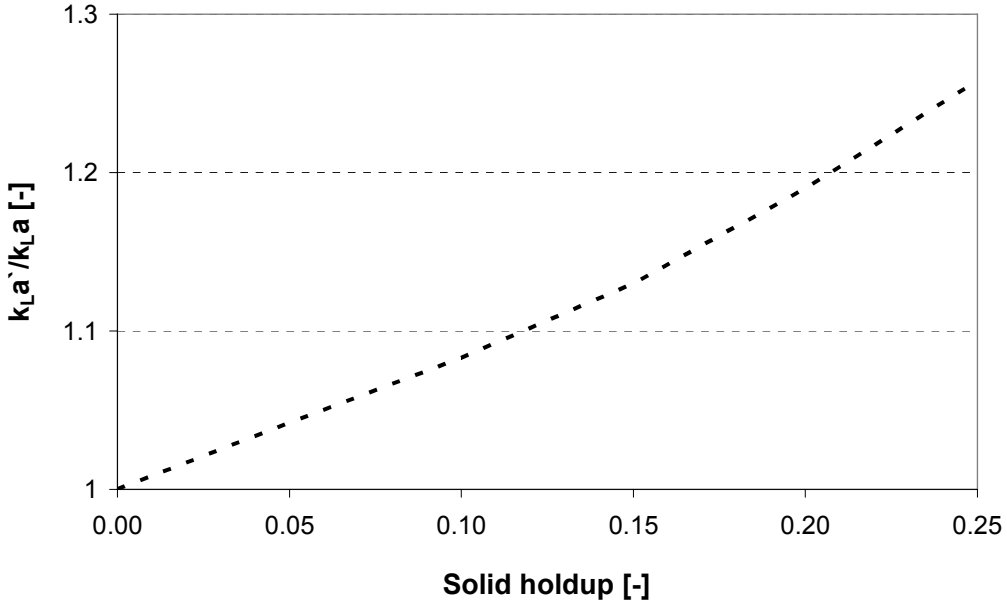

Figure 63: Relationship between the calculated $k_La´$, which takes account of intraparticle diffusion, and measured k_La with increasing gel like particle concentration (d_p = 1.71 mm)

The plot is based on the following mathematical calculation (11-24):

$$\frac{C}{C^*} = 1 - exp(-\beta' \cdot t) \cdot \left\{ \frac{p}{R} \cdot \left[(1 - \lambda \cot \lambda) \cdot \frac{exp(\beta' - \beta) \cdot t}{\beta' - \beta} - 2\lambda^2 \cdot \sum_{n=1}^{\infty} \frac{exp\left(\beta' - \frac{D_e \cdot n^2 \cdot \pi^2}{R^2} \right) \cdot t}{\left(n^2 \cdot \pi^2 - \lambda^2 \right) \left(\beta' - \frac{D_e \cdot n^2 \cdot \pi^2}{R^2} \right)} \right] + m \right\}$$

with

$$m = 1 - \left(\frac{p}{R} \right) \cdot \left(\frac{(1 - \lambda \cot \lambda)}{\beta' - \beta} - 2\lambda^2 \cdot \sum_{n=1}^{\infty} \frac{1}{\left(n^2 \cdot \pi^2 - \lambda^2 \right) \left(\beta' - \frac{D_e \cdot n^2 \cdot \pi^2}{R^2} \right)} \right) \qquad (11\text{-}25)$$

$$\lambda = \left(\frac{\beta \cdot R^2}{D_e} \right)^{0.5} \; ; \; p = \left(\frac{3 \cdot D_e \cdot \varepsilon_S}{R \cdot \varepsilon_L} \right) \; ; \; \beta' = \left(\frac{k_L' a}{\varepsilon_L} \right) \qquad (11\text{-}26)$$

The values of β are determined by least squares fitting of the experimentally obtained c vs. t curves.

11.10 John et al. (2006): A method for calculation of the relative velocity of gas bubbles in three-phase flows

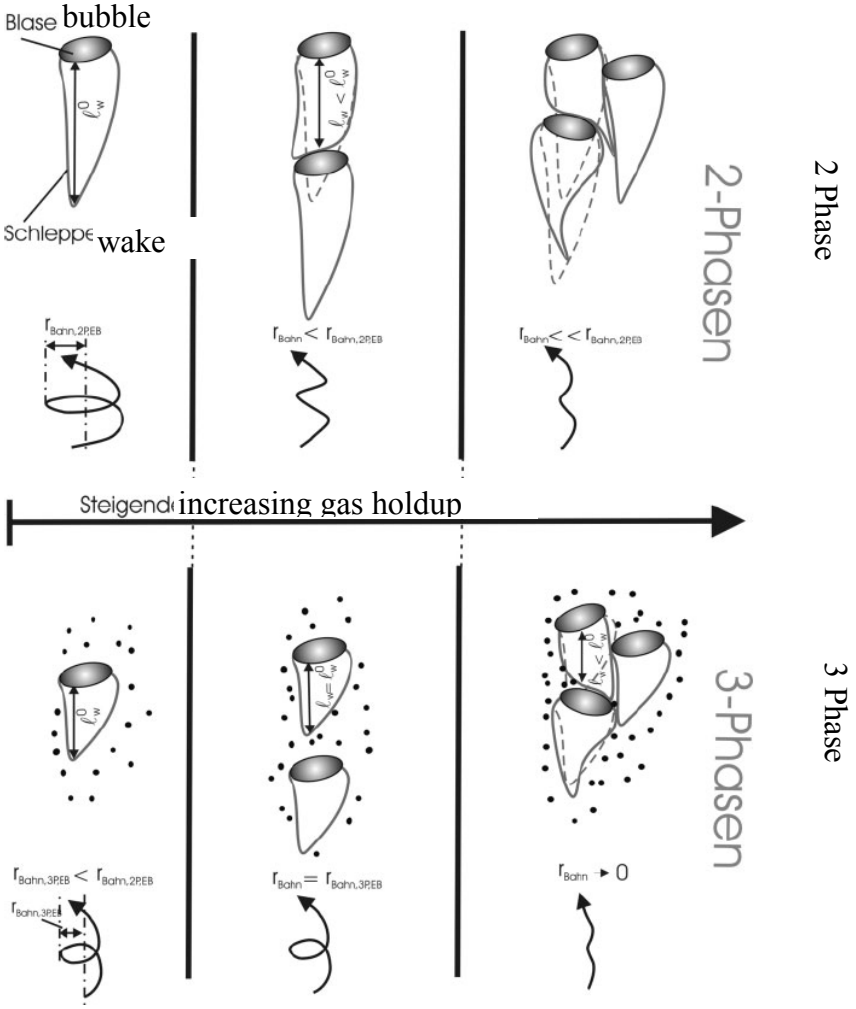

Figure 64: Graphical representation of the bubble rising and bubble wake behavior in two and three phase flow patterns

Table 19: Reactor specifications for oxygen transfer tests

	Reactor A, I fine bubble aeration.	Reactor A, II coarse bubble aeration	Reactor B, I fine bubble aeration only	Reactor B, II fine and coarse bubble aeration	Reactor C fine bubble aeration	Lab-scale column fine bubble aeration	Lab-scale column coarse bubble aeration
Diffuser type/ material	Plate/ membrane	Tube/ perforated	Tube/ membrane	Tube + plate/ membrane + perforated	Disc/ membrane	Disc/ membrane	Tube/ perforated
Number of orifices [-]	6,700	20	45,000	45,000 + 78	24,300	8,000	10
Riser surface [m^2]	0.45	0.45	2.52	2.52	0.088	0.15	0.15
Water volume [m^3]	2.6	2.6	3.15	3.15	1.00	0.10	0.10
Superficial gas velocity (*SGV*) [$cm^3_{Air}/(cm^2_{Superf} \cdot s)$]	0.25 – 0.80	0.25 – 0.80	0.04 – 0.14	(0.04 – 0.14) + 0.16	0.95 – 2.54	0.09 – 0.74	0.09 – 0.74
Specific slit aeration rate [$cm^3_{Air}/(slit \cdot s)$]	0.17 – 0.54	56 – 181	0.02 – 0.08	(0.02 – 0.08) + 52	0.03 – 0.09	0.02 – 0.14	14 – 112
Specific reactor aeration rate [$m^3_{Air}/(m^3_{reactor} \cdot h)$]	1.5 – 5.0	1.5 – 5.0	1.27 – 4.13	(1.27 – 4.13) + 4.60	3 – 8	5 – 40	5 – 40

Table 20: Gas chromatography-mass spectrometry (GC-MS) screening results in Greywater Experiments Part II

Substance	Unit.	Influent	Permeate *SRT* = 12 d	Permeate *SRT* = 80 d	Supernatant *SRT* = 12 d in operation	Supernatant *SRT* = 80 d in operation	Unit	Sludge *SRT* = 12 d in operation	Sludge *SRT* = 80 d in operation
Fatty acids									
C12	mg/L	20 – 200 (45)	n.d.	n.d.	n.d.	n.d.	mg/kg	n.d.	n.d.
C14	mg/L	5 – 50 (15)	n.d.	n.d.	n.d.	n.d.	mg/kg	1 – 10 (3.2)	n.d.
C15	mg/L	n.d.	n.d.	n.d.	n.d.	n.d.	mg/kg	n.d.	n.d.
C16	mg/L	5 – 50 (21)	n.d.	n.d.	0.5 – 5 (1.8)	n.d.	mg/kg	10 – 100 (27)	2 – 20 (15)
C18	mg/L	5 – 50 (22)	n.d.	n.d.	0.5 – 5 (2.3)	n.d.	mg/kg	5 – 50 (15	1 – 10 (6.9)

Table 21: Gas chromatography-mass spectrometry (GC-MS) screening results at an SRT of 2 d

No. 2	MBR I	*F/M* ratio: 0.23 kg *BOD*/(kg *MLVSS*·d)		*SRT*: 2 d				
Fatty acids	Unit	Influent	Permeate	Supernatant in operation	Supernatant 24 h aerated	Unit	Sludge in operation	Sludge 24 h aerated
C12	mg/L	0.2 - 2 (0.5)	n.d.	n.d.	n.d.	mg/kg	n.d.	n.d.
C14	mg/L	0.2 - 2 (0.6)	n.d.	n.d.	n.d.	mg/kg	0.5 – 5 (2.1)	0.2 – 2 (1.1)
C15	mg/L	n.d.	n.d.	n.d.	n.d.	mg/kg	0.5 – 5 (1.5)	n.d.
C16	mg/L	0.5 – 5 (3)	n.d.	0.05 - 0.5 (0.1)	n.d.	mg/kg	5 – 50 (23)	2 – 20 (9.6)
C18	mg/L	2 - 20 (10)	n.d.	0.05 - 0.5 (0.2)	n.d.	mg/kg	5 – 50 (37)	2 – 20 (12)

Table 22: Gas chromatography-mass spectrometry (GC-MS) screening results at an SRT of 8 d

No. 3	MBR I	*F/M* ratio: 0.17 kg *BOD*/(kg *MLVSS*·d)			*SRT*: 8 d				
Fatty acids	Unit	Influent	Influent (filtered)	Permeate	Supernatant in operation	Supernatant 24 h aerated	Unit	Sludge in operation	Sludge 24 h aerated
C12	mg/L	0.1 – 1 (0.5)	n.d.	n.d.	n.d.	n.d.	mg/kg	n.d.	n.d.
C14	mg/L	0.1 – 1 (0.6)	n.d.	n.d.	n.d.	n.d.	mg/kg	0.5 – 5 (1.9)	n.d.
C15	mg/L	0.05 - 0.5 (0.2)	n.d.	n.d.	n.d.	n.d.	mg/kg	n.d.	n.d.
C16	mg/L	2 - 20 (5.6)	0.05 - 0.5 (0.2)	n.d.	n.d.	n.d.	mg/kg	5 – 50 (20)	1 – 10 (6.3)
C18	mg/L	2 - 20 (11)	0.1 – 1 (0.6)	n.d.	n.d.	n.d.	mg/kg	5 – 50 (24)	2 - 20 (12)

Table 23: Gas chromatography-mass spectrometry (GC-MS) screening results at an SRT of 19 d

No. 5	MBR II	*F/M* ratio: 0.14 kg *BOD*/(kg *MLVSS*·d)			*SRT*: 19 d		
Fatty acids	Unit	Influent	Permeate	Supernatant in operation	Unit	Sludge in operation	Sludge 24 h aerated
C12	mg/L	0.5 – 5 (1.5)	n.d.	n.d.	mg/kg	n.d.	n.d.
C14	mg/L	0.5 – 5 (1.9)	n.d.	n.d.	mg/kg	0.5 – 5 (1.5)	n.d.
C15	mg/L	n.d.	n.d.	n.d.	mg/kg	n.d.)	n.d.
C16	mg/L	5 – 50 (15)	n.d.	0.5 - 5 (1.8)	mg/kg	5 – 50 (22)	0.5 – 5 (2.1)
C18	mg/L	5 – 50 (30)	n.d.	0.5 - 5 (3.9)	mg/kg	5 – 50 (26)	0.5 – 5 (2.2)

Table 24: Gas chromatography-mass spectrometry (GC-MS) screening results at an SRT of 23 d

No. 7	MBR II	*F/M* ratio: 0.13 kg *BOD*/(kg *MLVSS*·d)			*SRT*: 23 d		
Fatty acids	Unit	Influent	Permeate	Supernatant in operation	Unit	Sludge in operation	Sludge 24 h aerated
C12	mg/L	n.d.	n.d.	n.d.	mg/kg	n.d.	n.d.
C14	mg/L	0.05 – 0.5 (0.2)	n.d.	n.d.	mg/kg	n.d.	n.d.
C15	mg/L	n.d.	n.d.	n.d.	mg/kg	n.d.	n.d.
C16	mg/L	0.5 – 5 (2.8)	n.d.	n.d.	mg/kg	5 – 50 (18)	2 – 20 (15)
C18	mg/L	1 – 10 (4.5)	n.d.	n.d.	mg/kg	5 – 50 (26)	5 – 50 (22)

Table 25: Gas chromatography-mass spectrometry (GC-MS) screening results at an SRT of 36 d

No. 6	MBR I	*F/M* ratio: 0.09 kg *BOD*/(kg *MLVSS*·d)			*SRT*: 36 d		
Fatty acids	Unit	Influent	Permeate	Supernatant in operation	Unit	Sludge in operation	Sludge 24 h aerated
C12	mg/L	n.d.	n.d.	n.d.	mg/kg	n.d.	n.d.
C14	mg/L	0.05 – 0.5 (0.2)	n.d.	n.d.	mg/kg	n.d.	n.d.
C15	mg/L	n.d.	n.d.	n.d.	mg/kg	0.5 – 5 (3.4)	n.d.
C16	mg/L	0.5 – 5 (2.8)	n.d.	n.d.	mg/kg	5 – 50 (35)	2 – 20 (6.3)
C18	mg/L	1 – 10 (4.5)	n.d.	n.d.	mg/kg	5 – 50 (53)	5 – 50 (16)

Table 26: Gas chromatography-mass spectrometry (GC-MS) screening results at an SRT of45 d

No. 4	MBR I	*F/M* ratio: 0.07 kg *BOD*/(kg *MLVSS*·d)			*SRT*: 45 d		
Fatty acids	Unit	Influent	Permeate	Supernatant in operation	Unit	Sludge in operation	Sludge 24 h aerated
C12	mg/L	0.5 – 5 (1.5)	n.d.	n.d.	mg/kg	n.d.	n.d.
C14	mg/L	0.5 – 5 (1.9)	n.d.	n.d.	mg/kg	n.d.	n.d.
C15	mg/L	n.d.	n.d.	n.d.	mg/kg	n.d.	n.d.
C16	mg/L	5 – 50 (15)	n.d.	0.1 - 1 (0.4)	mg/kg	5 – 50 (26)	n.d.
C18	mg/L	5 – 50 (30)	n.d.	0.1 - 1 (0.6)	mg/kg	5 – 50 (30)	0.5 – 5 (1.5)

Table 27: Gas chromatography-mass spectrometry (GC-MS) screening results at an SRT of 46 d

No. 9	MBR II	*F/M* ratio: 0.06 kg *BOD*/(kg *MLVSS*·d)	*SRT*: 46 d
Fatty acids	Unit	Sludge in operation	Sludge 24 h aerated
C12	mg/kg	n.d.	n.d.
C14	mg/kg	1-10 (2.5)	n.d.
C15	mg/kg	1-10 (2.9)	n.d.
C16	mg/kg	5 – 50 (37)	5 – 50 (29)
C18	mg/kg	10 – 100 (52)	10 – 100 (56)

Table 28: Gas chromatography-mass spectrometry (GC-MS) screening results at an SRT of 73 d

No. 8	MBR I	*F/M* ratio: 0.04 kg *BOD*/(kg *MLVSS*·d)		*SRT*: 73 d		
Fatty acids	Unit	Influent	Influent (filtered)	Unit	Sludge in operation	Sludge 24 h aerated
C12	mg/L	0.02 – 0.2 (0.4)	n.d.	mg/kg	n.d.	n.d.
C14	mg/L	0.02 – 0.2 (0.8)	n.d.	mg/kg	n.d.	n.d.
C15	mg/L	n.d.	n.d.	mg/kg	n.d.	n.d.
C16	mg/L	1 – 10 (5.9)	0.01 - 0.1 (0.3	mg/kg	5 – 50 (18)	2 – 20 (13)
C18	mg/L	2 – 20 (13)	0.01 – 0.1 (0.5)	mg/kg	5 – 50 (29)	5 - 50 (16)

11.14 GC-MS screening results for influent with PAC addition

Table 29: GC-MS screening results for influent with PAC addition

Fatty acids	Unit	Influent	Influent	Influent + 1 g/L PAC	Influent + 1 g/L PAC
		raw	filtered	raw	filtered
C12	mg/L	0.5 - 5 (3)	n.d.	0.2 - 2 (1.2)	n.d.
C14	mg/L	1 - 10 (4.2)	n.d.	0.5 - 5 (2.1)	n.d.
C15	mg/L	0.2 – 2 (0.9)	n.d.	n.d.	n.d.
C16	mg/L	5 – 50 (30)	0.2 – 2 (1.4)	2 – 20 (14).	n.d.
C18	mg/L	10 – 100 (69)	1 – 10 (4.8)	5 - 50 (28)	n.d.

11.15 Volumetric mass transfer coefficients during wastewater experiments

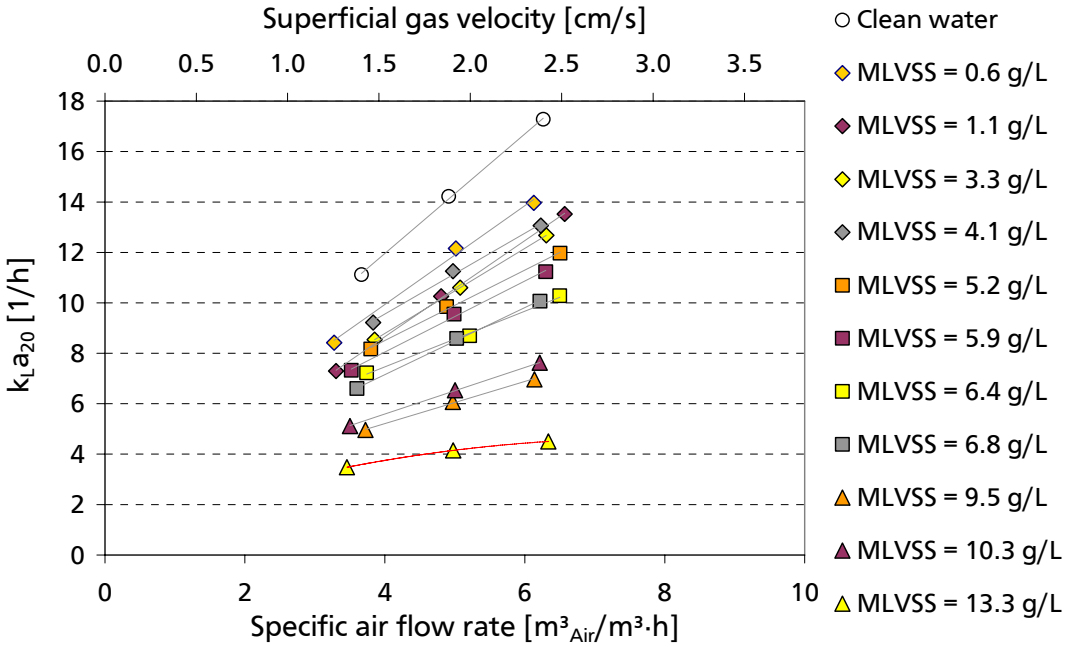

Figure 65: Volumetric mass transfer coefficients at different MLVSS concentrations (membrane bioreactor in operation)

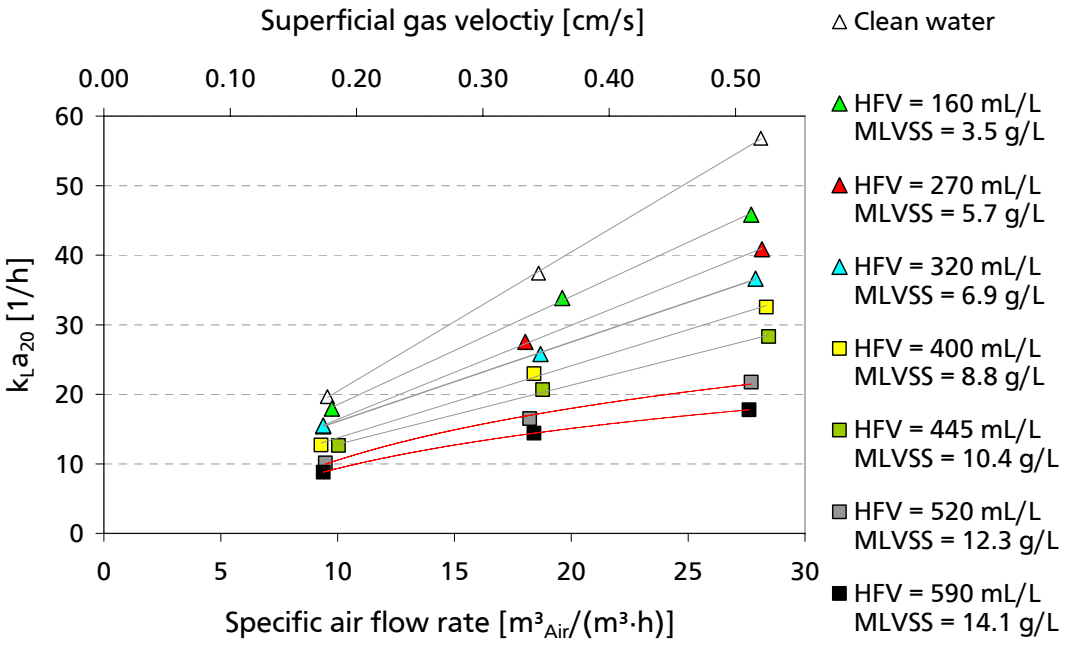

Figure 66: Volumetric mass transfer coefficients at different MLVSS concentrations measured using dilution of 24 h aerated sludge without influent (lab-scale column)

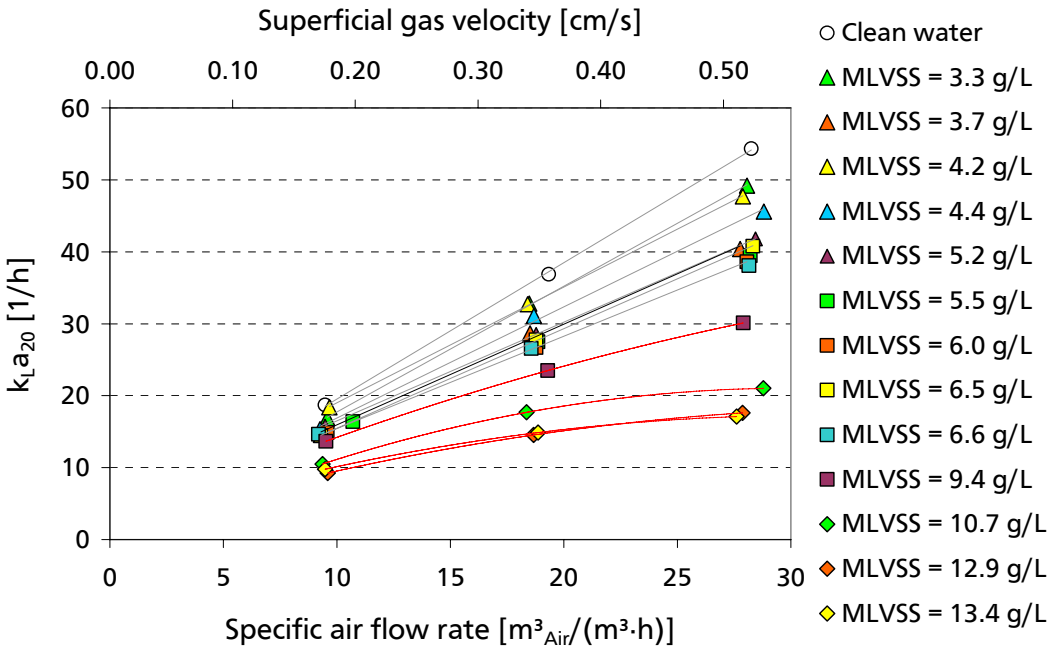

Figure 67: Volumetric mass transfer coefficients at different MLVSS concentrations (lab-scale column)

11.16 Volumetric mass transfer coefficients during iron hydroxide experiments

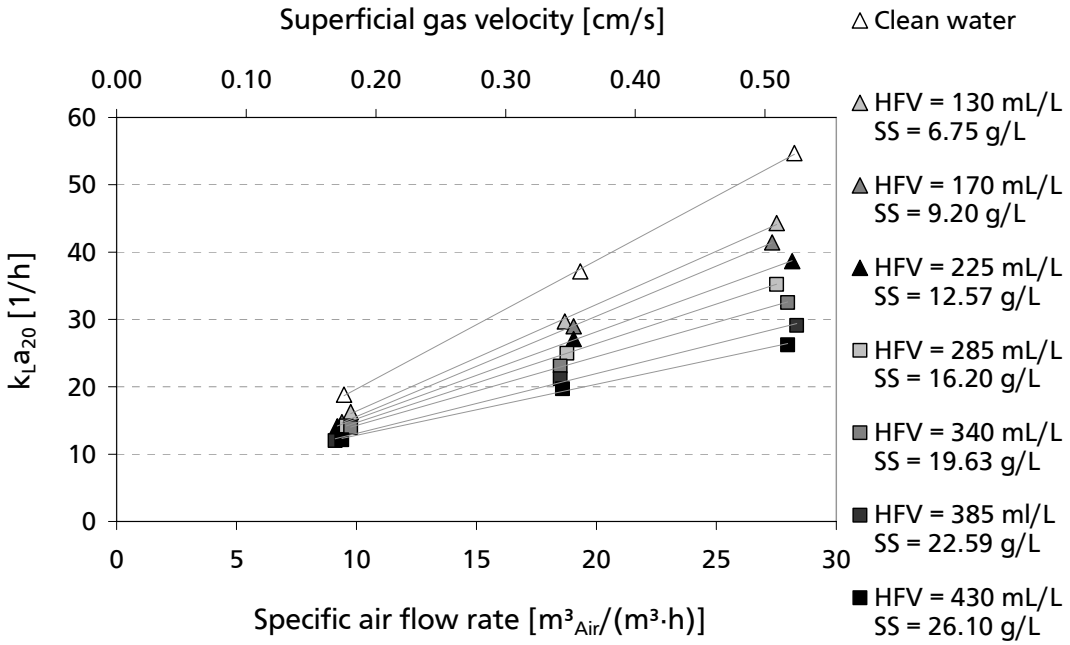

Figure 68: Volumetric mass transfer coefficient during iron hydroxide experiments at different HFV and suspended solids concentrations (fine bubble aeration)

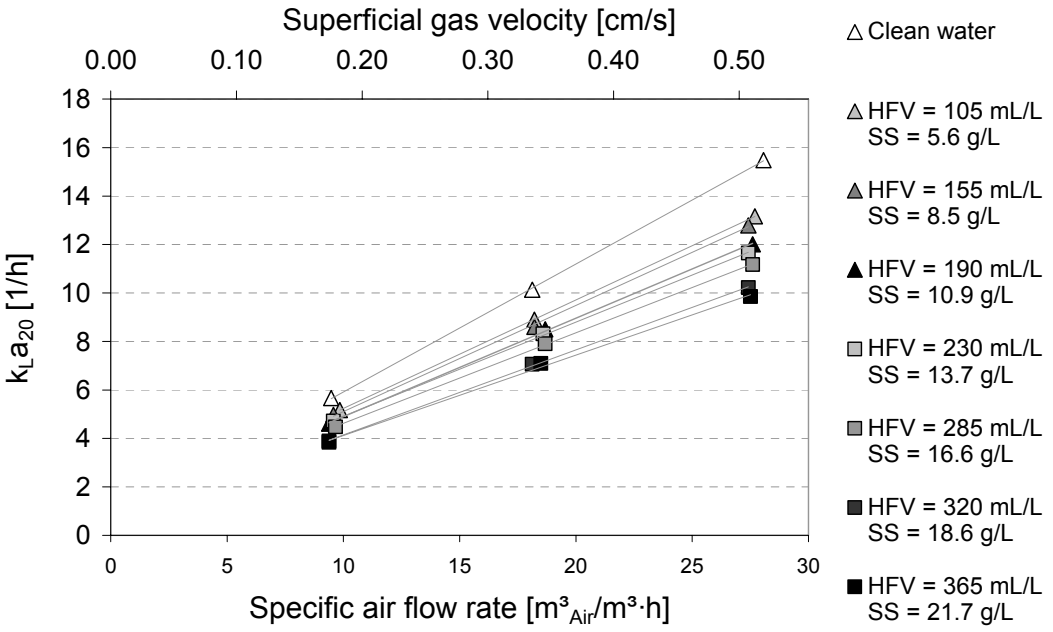

Figure 69: Volumetric mass transfer coefficients during iron hydroxide experiments at different HFV and suspended solids concentrations (coarse bubble aeration)

11.17 α-factors at different air flow rates

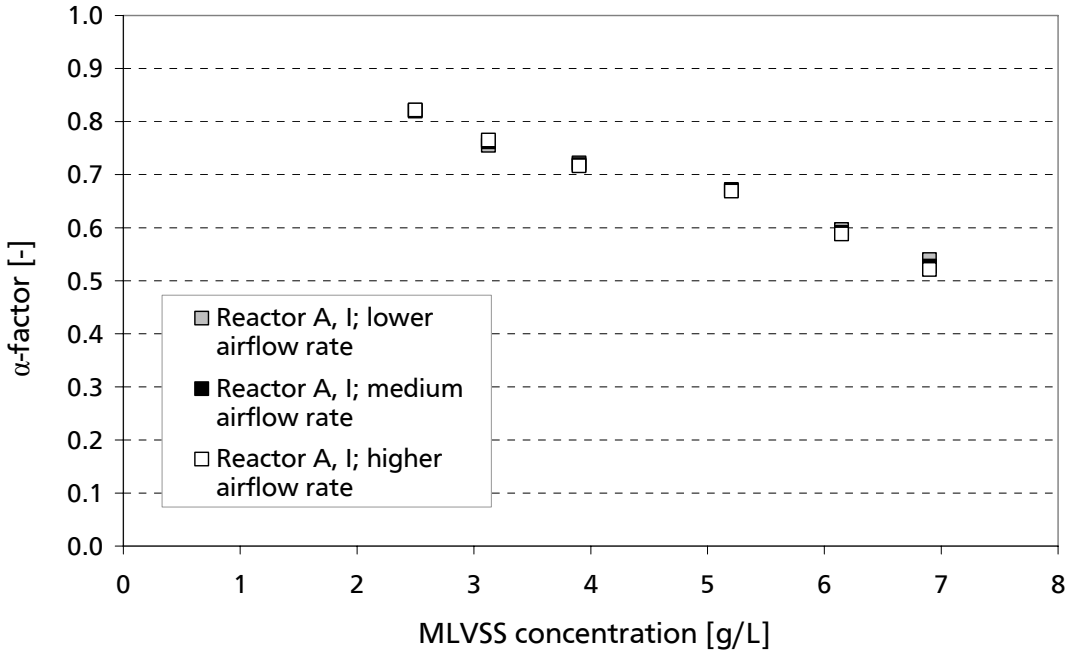

Figure 70: α-factors at different air flow rates during Greywater Experiments Part I; reactor A equipped with fine bubble aeration device

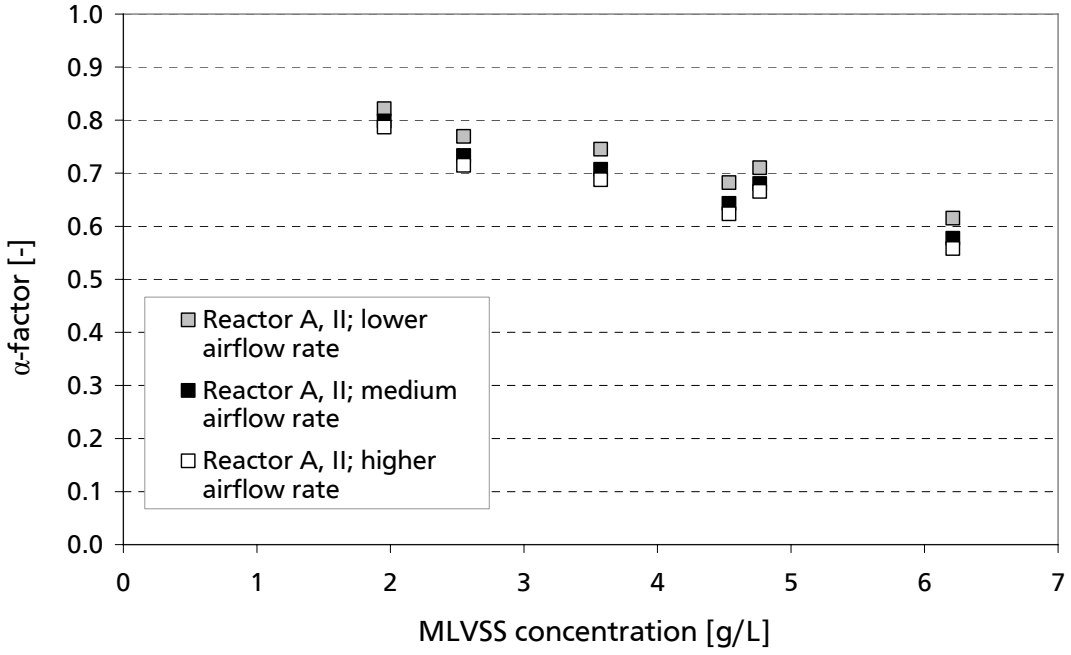

Figure 71: α-factors at different air flow rates during Greywater Experiments Part I; reactor A equipped with coarse bubble aeration device

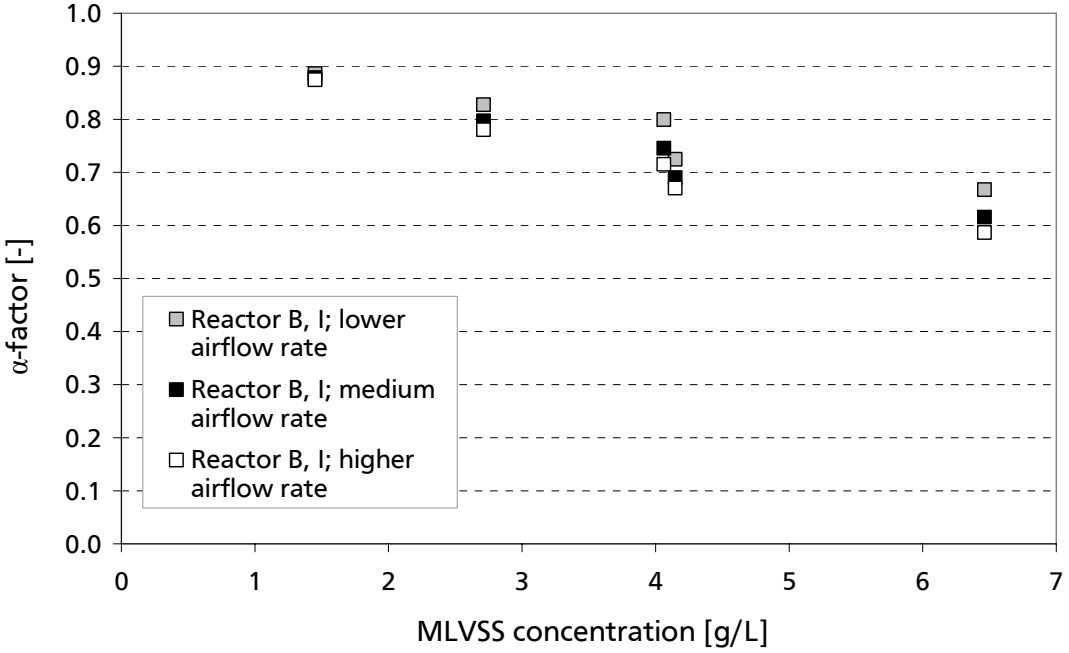

Figure 72: α-factors at different air flow rates during Greywater Experiments Part I; reactor B (only fine bubble aeration)

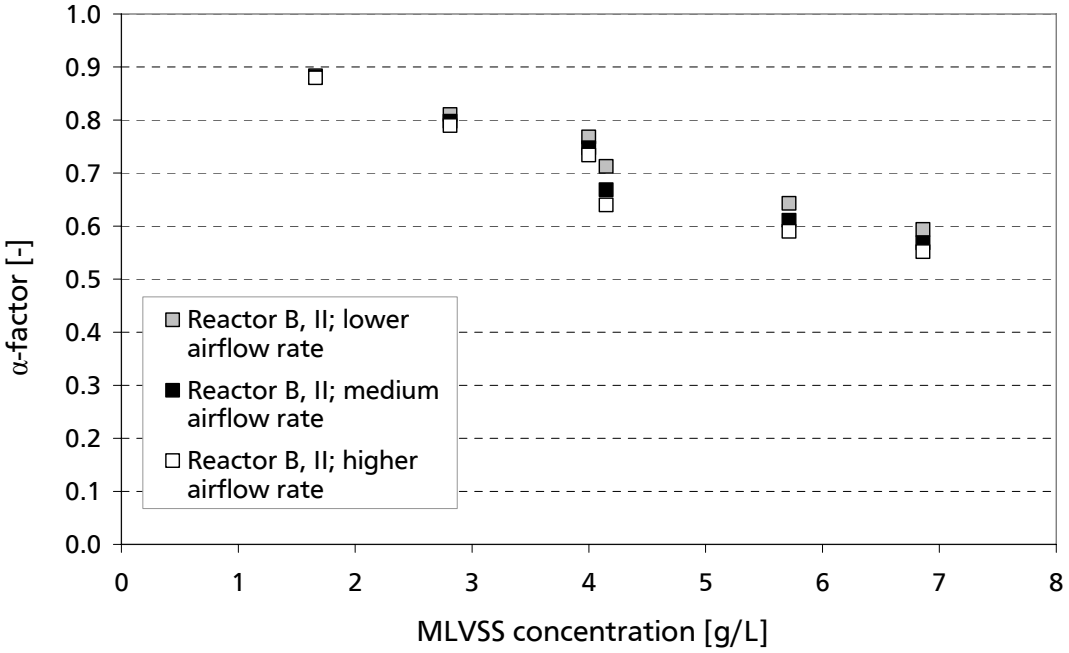

Figure 73: α-factors at different air flow rates during Greywater Experiments Part I; reactor B (fine bubble and coarse bubble aeration)

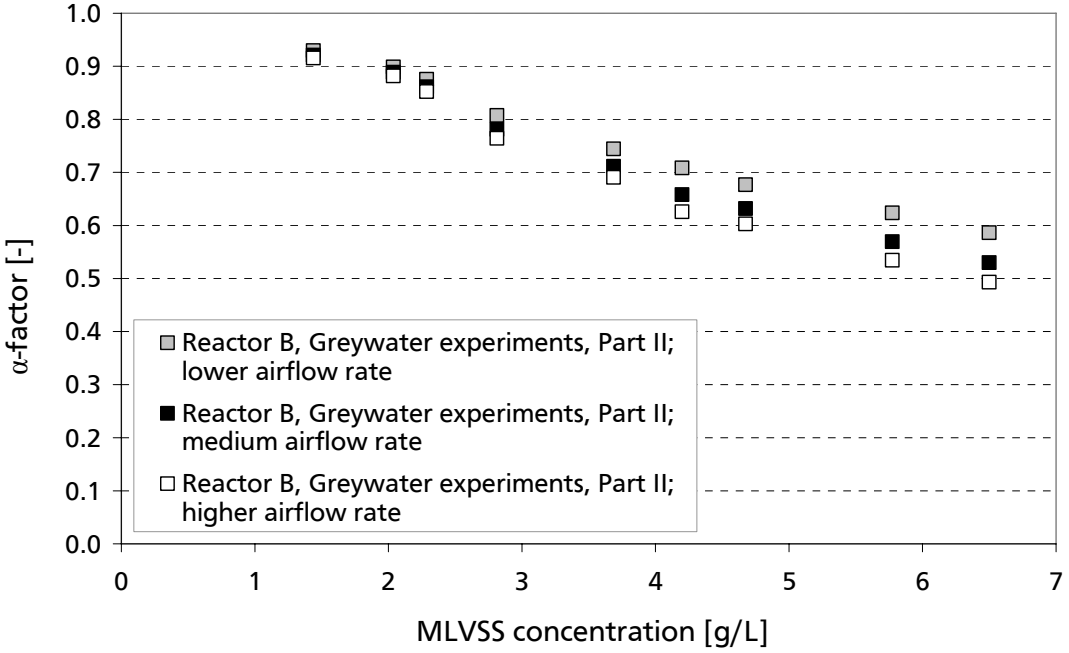

Figure 74: α-factors at different air flow rates during Greywater Experiments Part II; reactor B (fine bubble and coarse bubble aeration)

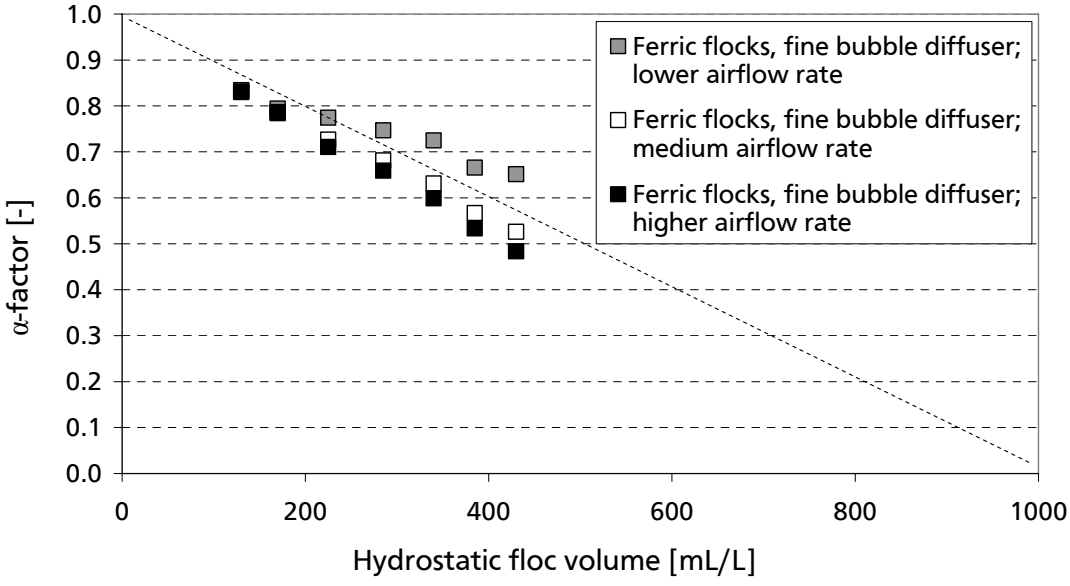

Figure 75: α-factors at different air flow rates during iron hydroxide experiments (fine bubble aeration)

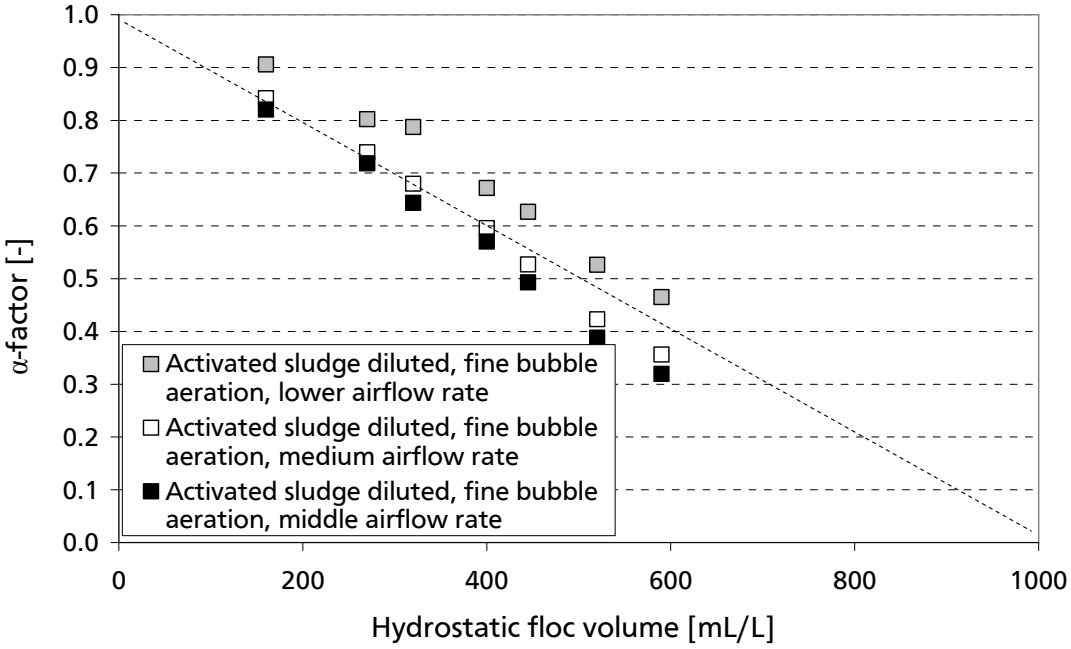

Figure 76: α-factors at different air flow rates with diluted activated sludge (fine bubble aeration)

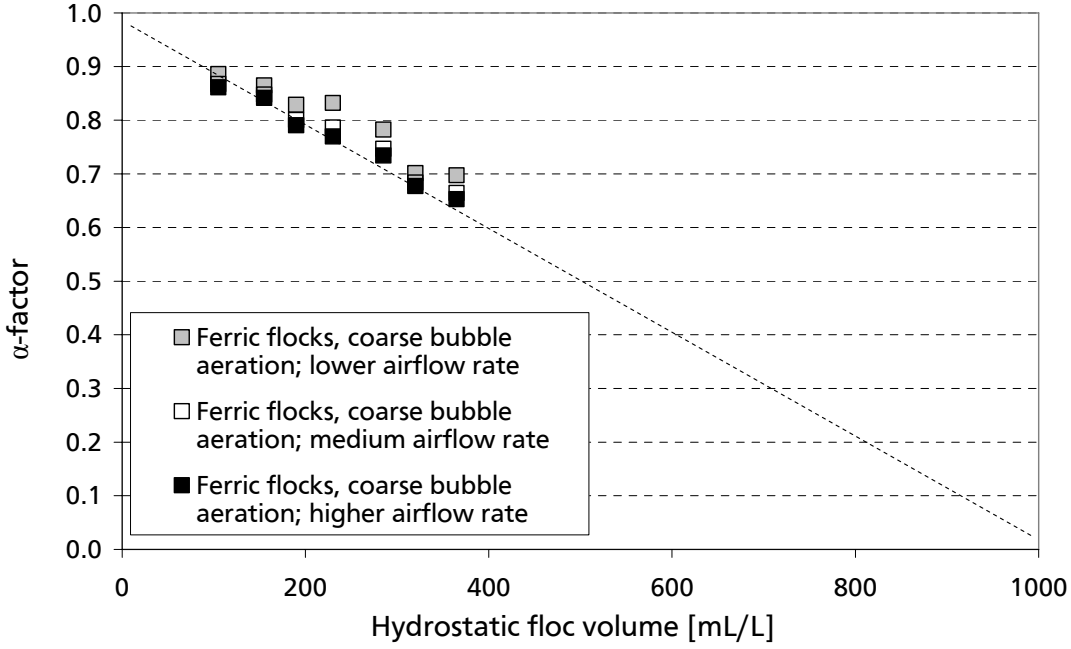

Figure 77: α-factors at different air flow rates during iron hydroxide experiments (coarse bubble aeration)

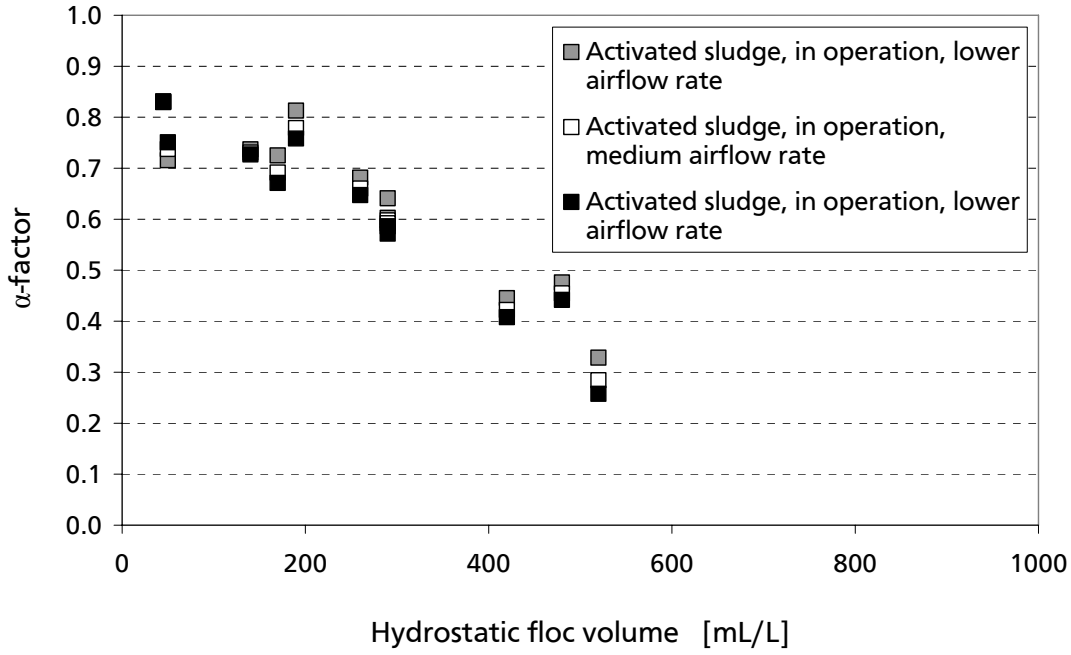

Figure 78: α-factors at different air flow rates with activated sludge in reactor C during operation (fine bubble aeration)

11.18 COD load to floc ratio

The *COD* load to floc ratio (Figure 79) is calculated by deviding the hourly *COD* load by the hourly mass of sludge which is recycled. It is based on the following assumptions:

- Inhabitant-specific flow rate = 120 L/(C·d)
- Inhabitant-specific *COD* load after preliminary sedimentation = 90 g/(C·d)
- *MLSS* concentration in the return sludge = 8 g/L and its flow is equivalent to the influent flow
- *MLSS* concentration in the internal recirculation = 4 g/L and the flow is 4 times the influent flow
- The variation of the hourly *COD* load is pictured in Figure 79. It is assumed that the *COD* load is proportional to the variation of wastewater flow during the day.

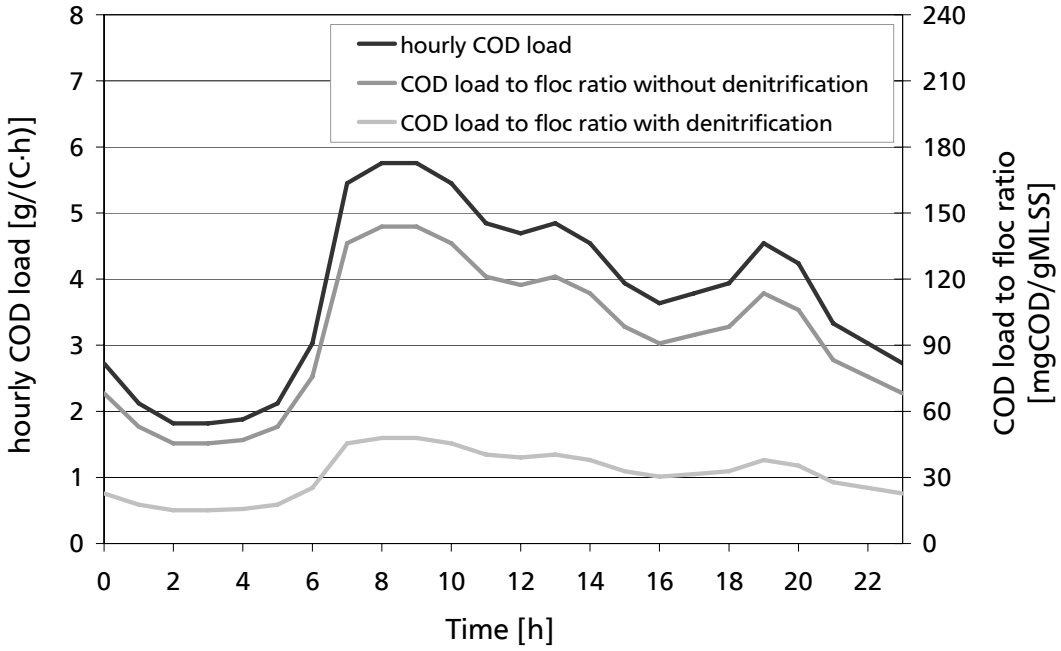

Figure 79: Hourly variation of COD load and COD load to floc ratio with and without denitrification

Figure 80 and Figure 81 illustrate the different recycling flows for a wastewater treatment plant with and without internal recirculation required for denitrification.

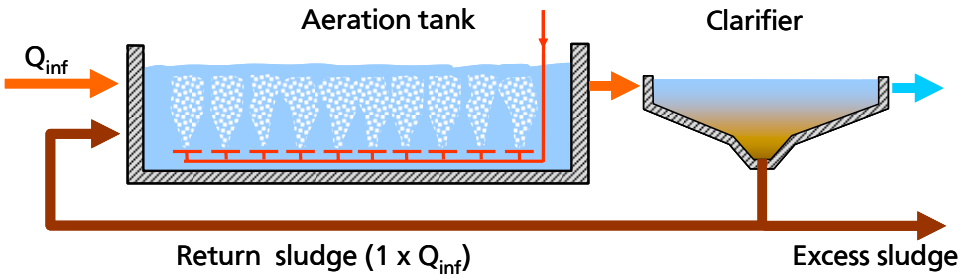

Figure 80: Sketch of an activated sludge plant with carbon removal and nitrification

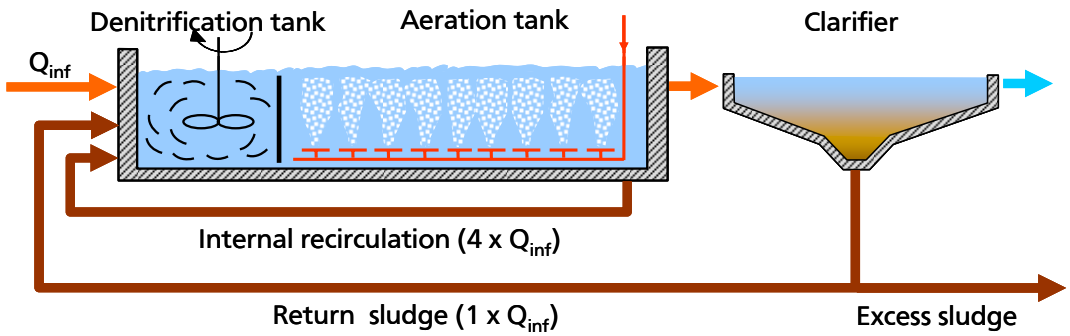

Figure 81: Sketch of an activated sludge plant with denitrification

11.19 Relationship between SRT, MLVSS and α-factor

Linear regression was used to relate the α-factor to the *SRT* (Figure 82) and *MLVSS* concentration (Figure 83).

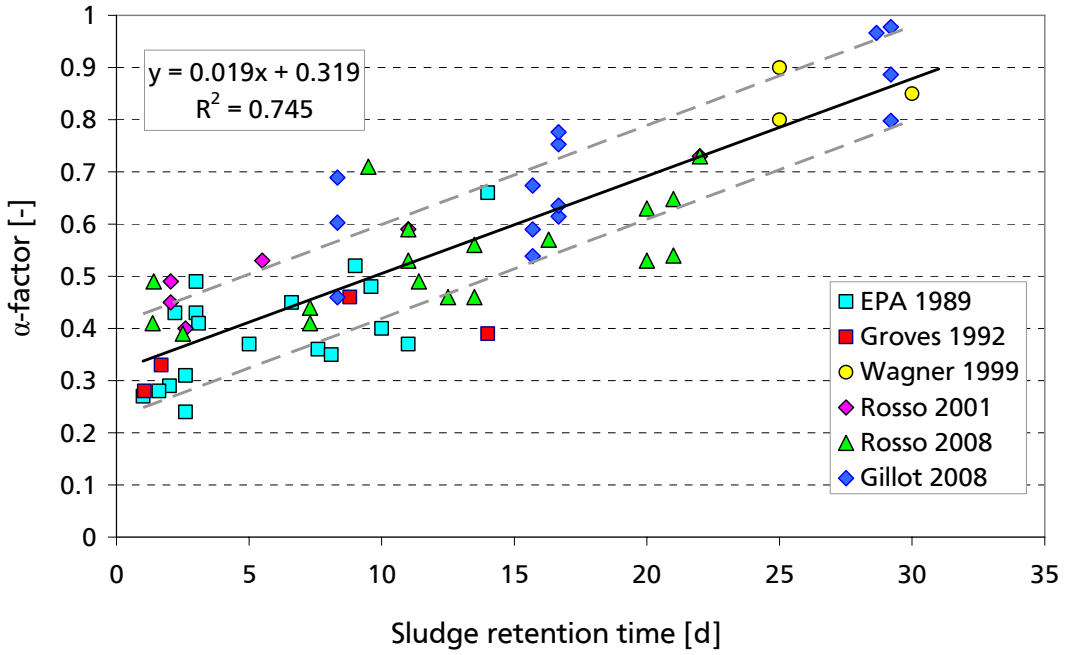

Figure 82: linear regression of α-factor and SRT

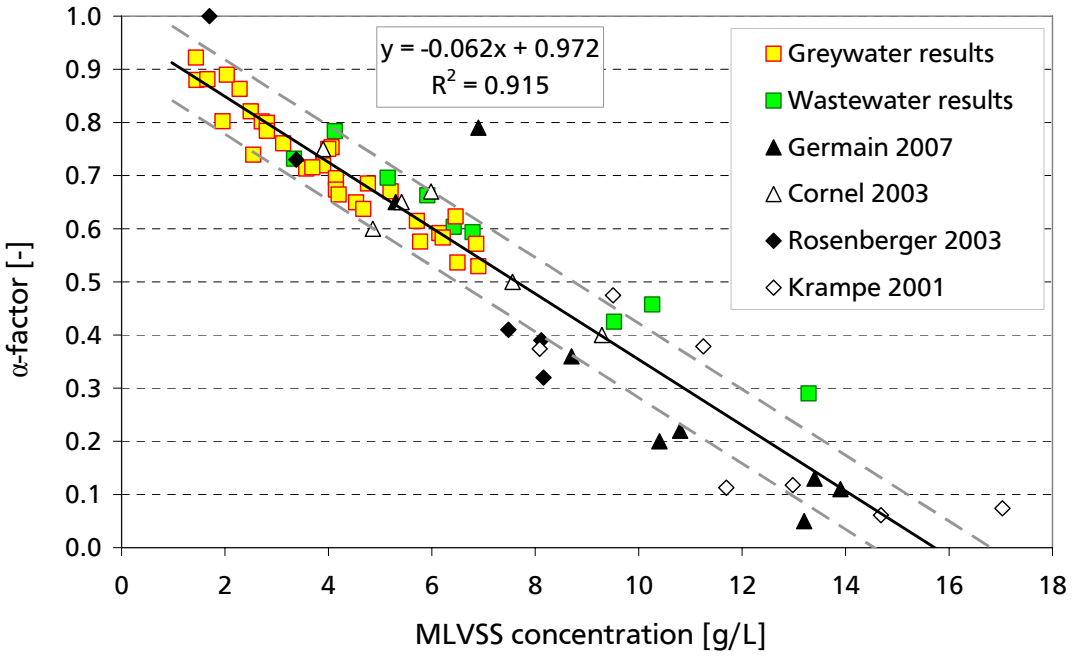

Figure 83: linear regression of α-factor and MLVSS concentration

In the first case the stability index is 0.745 and the standard deviation was ± 0.093. However the equation still includes the effect of the floc volume, since all measurements have been performed with activated sludge at a certain sludge concentration. Assuming an average *MLVSS* concentration of 3 g/L (α-factor = 0.786), and adjusting the trend line equation in Figure 82, which still incorporates the effect of the MLVSS concentration by parallel translation to a hypothetical MLVSS value of "0", the following equation, which only describes the effect of the SRT, is derived:

$$\alpha - factor = 0.019 \cdot SRT + 0.533 \quad \pm 0.093 \qquad (11\text{-}27)$$

with

SRT [d] Sludge retention time [1 – 30 d]

In the second case, the dependency of the α-factor on the *MLVSS* concentration, the stability index is 0.915 and the standard deviation was ± 0.07.

$$\alpha - factor = -0.062 \cdot MLVSS + 0.972 \quad \pm 0.070 \qquad (11\text{-}28)$$

with

MLVSS [g/L] Mixed liquid volatile suspended solids [1 – 12 g/L]

If both equations are summarized, the α-factor can be approximated with the following formula:

$$\alpha - factor = 0.51 - 0.062 \cdot MLVSS + 0.019 \cdot SRT \quad \pm 0.114 \qquad (11\text{-}29)$$

This equation is also used for the illustration of Figure 44

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*WA*R 26	Naturnahe Abwasserbehandlungsverfahren im Leistungsvergleich - Pflanzenkläranlagen und Abwasserteiche -. 9. Wassertechnisches Seminar am 07.11.1985, TH Darmstadt, 1986	vergriffen
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*WA*R 119	Herr, Christian: Innovative Analyse und primärseitige Prozeßführungsoptimierung thermischer Abfallbehandlungsprozesse – am Beispiel der Mülleingangsklassifizierung bei der Rostfeuerung. Dissertation, FB 13, TU Darmstadt, 2000	33,20 €

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